

Introductory Remarks

The present mini-symposium is the fourth one organized in the field of polymer engineering and science by the Industrial Materials Research Institute of the National Research Council of Canada (IMRI-NRCC). The first two, Thermodynamics of Liquids and Polymer Blends '81-, have been already published in *Polymer Engineering and Science* (mid-February issue). The third, Composites '81, is in print (in *Polymer Composites*).

Since the early days of its foundation, IMRI has established three priority areas in the field of polymeric materials: blends, composites, and CAD/CAM. The present mini-symposium fits under the umbrella of the last of these areas. Thus, the activities of the Institute in mathematical modeling and computer simulation of plastics processing represent a link in a chain of activities, including: the development of a data bank for polymer and plastics properties; modeling and simulation; studies of the microstructure and performance of manufactured articles; computer packages for the basic design parameters for molds, dies, screws, etc.; and computer packages for controlled manufacturing capabilities. Obviously, the task is vast, and what is needed will be beyond the capabilities and competence of a single institution or group of people. Therefore, it is hoped that the various interested organizations will coordinate their efforts to maximize benefits to the plastics industry. Communication and the exchange of ideas in symposia like the present one play a significant role in this coordination effort.

The Mini-Symposium papers selected for this issue deal with a cross-section of important commercial plastics manufacturing operations: extrusion, injection molding, and blow molding. Both computer simulation and control topics are covered. Moreover, a quick glance at the contents of the various papers shows that they involve a broad range of polymer engineering and science subjects; e.g., rheology, thermodynamics, fluid mechanics, heat transfer, crystallization kinetics, etc. Therefore, it is hoped that the readers of the Journal will find the material interesting and useful.

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Editor's Note:

The following four papers were presented during the First Mini-Symposium on Computer Simulation of Polymer Processing-Computer Simulation-82, organized and sponsored by the Industrial Materials Research Institute of the National Research Council of Canada (IMRI-NRCC) on February 9, 1982 in Montreal.

Computer simulation, which is closely associated with mathematical modeling of plastics processing, is one of the main areas of activity at IMRI. In fact, its activity in this area is part of a more general and extensive program to establish competence in CAD/CAM, in aid of the Canadian plastics industry.

During the last decade, computer simulation of important plastics manufacturing operations, like extrusions and injection molding, has become an important field of activity among polymer engineers and scientists. Such interest is not surprising, since process simulation finds many applications in process optimization and control, in addition to the optimization of resin selection and die and mold design, in order to improve production economics and product quality. It is expected that computer simulation will continue to gain prominence during the present decade as a result of the expanded use of microprocessors and computers in conjunction with the control and supervision of plastics operations. Other incentives include material and energy saving applications in computer-aided die and mold design, the availability of powerful finite-element schemes and visco-elastic constitutive equations that permit the treatment of the processing behavior of complex materials in complicated dies and molds, and the development of procedures to relate thermomechanical history of the resin during processing to microstructure and ultimate properties of the final product.

Three of the four articles appearing in this issue deal with computer simulation of the three most important plastics manufacturing operations: extrusion (Agur and Vlachopoulos), injection molding (Kamal and Lafleur), and blow molding (Ryan and Dutta). The fourth paper (Costin, Taylor, and Wright) relates to the very important area of process dynamics and control of the extrusion operation. The proceedings of the Mini-Symposium, including a transcript of discussion, are part of an internal NRCC publication.

Musa R. Kamal,
Guest Editor

Computer Simulation of Injection Molding

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The injection-molding process consists of three consecutive stages: filling, packing, and cooling. In order to obtain some insight into the phenomena involved in the process, and particularly in order to evaluate the moldability of certain resins and to predict the microstructure and properties of products molded therefrom, a number of workers have employed a variety of techniques based on mathematical simulation of the process. Mathematical simulation involves writing the relevant continuity, momentum, and energy equations governing the system, with appropriate boundary and initial conditions representing the prevailing conditions in the cavity and delivery channels. In order to obtain meaningful solutions to the above equations, detailed information is required regarding the thermodynamic, thermal, and rheological properties of the resin. Moreover, the prediction of the microstructure and ultimate properties of the molded article requires a knowledge of the morphological, crystallization, and orientation phenomena that take place under the influence of the thermo-mechanical history experienced by the resin. The complexity of the equations involved results in the utilization of a number of simplifying assumptions and the resort to computer simulation and numerical solutions of these equations. A variety of numerical schemes based on finite difference and finite element methods has been employed by various researchers.

INTRODUCTION

Injection molding is a very important industrial process for the manufacturing of plastics objects. The injection molding cycle is composed of three stages: filling, packing, and cooling. During filling, the molten polymer, which is produced by the shearing action of a rotating screw combined with external heating, is introduced into the mold. After filling, extra material is packed under high pressure to compensate for shrinkage as the material cools. After the injection pressure is removed, cooling continues, and the pressure decreases.

Figure 1 is a schematic of an injection-molding pressure-time cycle. The ultimate properties of a molded part, obtained by injection molding, depend on material and process parameters. The resin properties, mold geometry, and molding conditions, which give rise to the thermomechanical history of the resin, determine the microstructure distribution and, there-

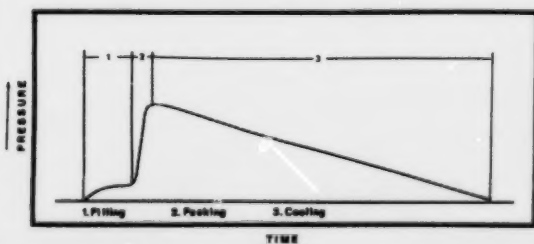


Fig. 1. Variation of pressure with time in injection molding.

fore, the ultimate properties of the molded article, as depicted in Fig. 2. Accordingly, computer simulation of the injection-molding process should incorporate relationships between resin properties, machine design, molding conditions, and the development of microstructure in order to provide information regarding the behavior of the material during molding and the ultimate properties of molded articles.

In this article, we attempt to outline some of the recent significant developments associated with computer simulation of the thermoplastics injection-molding process.

GENERAL CONSIDERATIONS AND EQUATIONS

A realistic simulation of the injection-molding process should be based on a model capable of describing the thermomechanical history experienced by the ma-

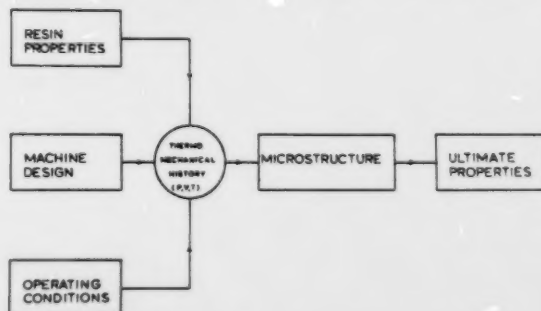


Fig. 2. Components of the plastics processing system.

terial during molding, including moldability parameters (such as pressure drop in the delivery system and cavity and melt front advancement during cavity filling), as well as the microstructure of the final product (such as the distributions of crystallinity, morphology, residual stresses, and orientation). Moreover, it should yield predictions regarding the ultimate properties of the system; e.g., optical and mechanical properties. Thus, a complete model should serve the dual purpose of evaluating both moldability and product quality.

Most of the available work regarding the simulation of the injection-molding process (filling, packing, and cooling) has been carried out and tested in conjunction with semicircular and rectangular cavities (1-3). This is probably due to the limitations of the finite difference schemes that are usually employed in solving the relevant equations. More recently, finite element methods have been employed. With these methods, it should be possible to obtain realistic simulation of injection molding in more complex cavities. Moreover, most available models of the injection-molding process have been based on viscous-flow considerations. It would be more realistic to employ a viscoelastic constitutive equation in order to obtain more accurate predictions of melt behavior and product quality.

Finally, a complete model of the injection-molding process must deal with all three stages of the process: filling, packing, and cooling. Although substantial and significant information may be deduced on the basis of the analysis of filling alone, as in the case in much of the available work, important moldability and product quality considerations depend heavily on phenomena occurring during the packing and cooling stages.

Filling Stage

The filling stage can be considered in two parts: firstly, the flow of the melt from the nozzle to the cavity and, secondly, the filling of the cavity.

Delivery channels. The delivery system consists of the nozzle region of the injection barrel, the mold sprue, the runner system, and the gate. Each of these elements of the system performs well-defined functions and affects the molding operation. The sprue, usually a short, diverging, conical channel, is the main pathway to the mold, connecting the nozzle and the runner system. One of its major characteristics is that it offers little resistance to the flow. The function of the runner system is to deliver the hot melt to the cavity with the minimum pressure drop. Relatively slow cooling is also important to avoid premature solidification. The gate controls the flow of polymer melt into the cavity. A narrow gate is desirable in order to facilitate the separation of the molded part from the runner system.

Models developed by Williams and Lord (4) and by Tadmor and Gogos (5) have dealt with the flow in delivery channels. However, simple volumetric flow rate-pressure drop relationships can be used, with some simplifying assumptions, to simulate the flow of the polymer melt in the delivery channels.

Hydrodynamics of Cavity Filling. After the molten polymer has traversed the delivery channels and

crossed the gate, the process of filling the cavity begins. The filling stage is concerned with the transient, nonisothermal flow of a compressible, viscoelastic fluid. The polymer melt is partially solidified during flow due to the temperature difference between the melt and the wall, the temperature at the wall being below the solidification temperature of the polymer.

Flow visualization studies of cavity filling have been reported in the literature. The first reported study was made by Spencer and Gilmore (6), who have studied visually the filling of the mold and derived an empirical equation for the determination of the filling time. Other early important flow visualization and tracer studies include the contributions of Ballman, *et al.* (7), and Rielly and Price (8).

Various analyses and models of the fluid mechanics of injection molding have been published. Early contributions include the empirical work of Spencer and Gilmore (6) and Ballman, *et al.* (7). In the early seventies, some authors began to analyse the mold-filling process as a problem of combined transport of momentum and energy. The transport phenomena approach has been applied to this transient and nonisothermal flow problem by many workers. Since the resulting system of differential equations is rather complex, various researchers have employed a variety of physical assumptions to simplify the mathematical treatment.

Harry and Parrott (9) coupled one-dimensional flow analysis with a heat-balance equation for a rectangular cavity in one of the first transport phenomena models. Basov and Felipchuk (10) used the same flow equations but used a different thermal approach using heat conduction equations for the liquid and solid phases. Kamal and Kenig (1) and Berger and Gogos (11) worked on the filling of a disc mold using the assumptions of a radial creeping flow.

For the analysis of the filling stage, a rectangular cavity may be divided into three regions, as shown in Fig. 3. In region 1, near the gate, the flow is radial until the flow front reaches the wall. Away from the gate, region 2, the flow is characterized by a dominant axial ve-

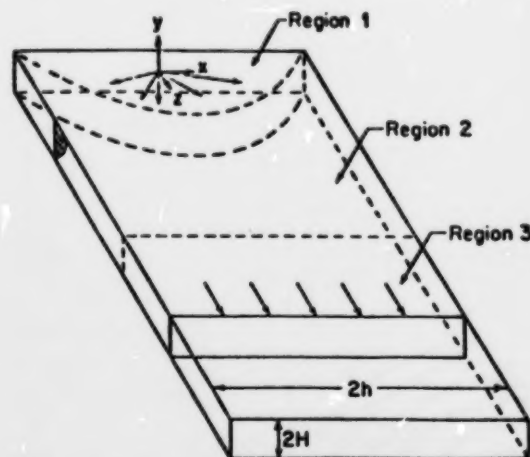


Fig. 3. Schematic representation of the flow patterns during the filling.

locity component. In region 3, called the front region, the melt acts differently; near the front, the melt, channeling through the center, seems to move out toward the cavity walls, as shown in Fig. 4. This phenomenon has been referred to as "fountain flow" by many workers.

The work of Richardson (12), suggesting that lubrication theory may be applied in many mold cavities, has been used by some workers in the modeling of cavity filling. Broyer, Gutfinger, and Tadmor (13) suggested that the flow in a narrow gap mold is a two-dimensional, fully developed creeping flow (Hele-Shaw-type flow). The following continuity and momentum equations, written in Cartesian coordinates, describe the flow field:

$$\begin{aligned} \frac{\partial V_x}{\partial x} + \frac{\partial V_y}{\partial y} &= 0 \\ -\frac{\partial P}{\partial x} - \frac{\partial \tau_{xx}}{\partial z} &= 0 \\ -\frac{\partial P}{\partial y} - \frac{\partial \tau_{xy}}{\partial z} &= 0 \end{aligned} \quad (1)$$

White (14) used the same set of equations to describe the flow in the intermediate region of the mold (region 2, Fig. 3). Hieber and Shen (15) employed the generalized Hele-Shaw flow for the modeling of the filling process using a finite-element numerical technique. The application of fully developed Hele-Shaw flow gives rise to errors in the entrance region and is also unsatisfactory in the representation of the front region. In an attempt to develop a model to represent the entry and the fully developed regions, some assump-

tions, less restrictive than for the Hele-Shaw flow, have to be used in regard to the geometry of the cavity and the fluid.

For the modeling of the flow phenomena of a polymer melt inside a cavity, the equations of conservation of mass, momentum, and energy may be written as follows:

Continuity:

$$\frac{D\rho}{Dt} = -\rho(\nabla \cdot \vec{v})$$

Momentum:

$$\rho \frac{D\vec{v}}{Dt} = -\nabla p - [\nabla \cdot \vec{\tau}] + \rho \vec{g} \quad (2)$$

Energy:

$$\rho C_v \frac{DT}{Dt} = (\nabla \cdot \vec{q}) - T \left(\frac{\partial P}{\partial T} \right) \rho (\nabla \cdot \vec{v}) - (\vec{\tau} \cdot \nabla \vec{v})$$

As a first step, it is possible to develop a set of assumptions that are, for the case of a non-Newtonian fluid flowing in a thin, rectangular cavity, physically representative of the process. These assumptions, used by almost every worker in the modeling of the cavity-filling process, lead to the simplification of the equations of mass, momentum, and energy without significant loss of generality of the treatment. The assumptions are listed below.

- The fluid motion is laminar.
- Body forces are negligible.
- The unsteady-state terms in the momentum and continuity equations are neglected in view of the comparatively long duration of the flow.
- There is no velocity component in the z direction (except near the front).

With these assumptions, the above equations take on the following forms (considering isothermal case):

Continuity

$$\frac{\partial}{\partial x} (\rho V_x) + \frac{\partial}{\partial y} (\rho V_y) = 0$$

Motion

$$\rho \left[V_x \frac{\partial V_x}{\partial x} + V_y \frac{\partial V_x}{\partial y} \right] = -\frac{\partial P}{\partial x} - \left[\frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z} \right] \quad (3)$$

$$\begin{aligned} \rho \left[V_x \frac{\partial V_y}{\partial x} + V_y \frac{\partial V_y}{\partial y} \right] &= -\frac{\partial P}{\partial y} - \left[\frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} + \frac{\partial \tau_{zy}}{\partial z} \right] \\ 0 &= -\frac{\partial P}{\partial z} - \left[\frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{yz}}{\partial y} + \frac{\partial \tau_{zz}}{\partial z} \right] \end{aligned}$$

At this point, two alternatives are available: to solve numerically the set of equations described above or to formulate more assumptions to simplify the equations. However, the introduction of any other simplifications would probably lower the quality and utility of the solution.

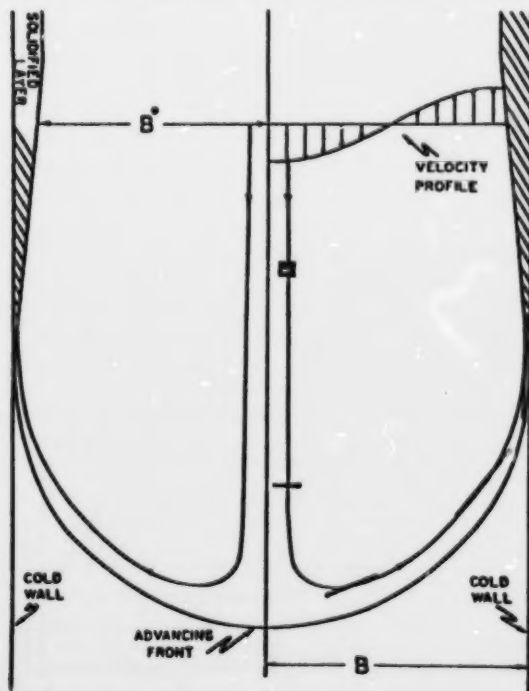


Fig. 4. Front region.

An assumption that is often used in the literature for polymeric systems is that viscous forces are considerably greater than the inertia forces (creeping flow). Pressure forces are then balanced by the viscous forces, and the equations of motion are reduced to:

$$\begin{aligned}\frac{\partial P}{\partial x} &= - \left[\frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z} \right] \\ \frac{\partial P}{\partial y} &= - \left[\frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} + \frac{\partial \tau_{zy}}{\partial z} \right] \\ \frac{\partial P}{\partial z} &= - \left[\frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{yz}}{\partial y} + \frac{\partial \tau_{zz}}{\partial z} \right]\end{aligned}\quad (4)$$

Further simplifications will lead to the Hele-Shaw flow described earlier.

Packing Stage

After the filling of the cavity is complete, when the flow front impinges against the dead end of the cavity, an additional amount of material is forced into the cavity to minimize the effect of shrinkage due to cooling. The packing stage is illustrated in Fig. 1, which shows a typical pressure-vs.-time profile (16). After the cavity has been filled, a rapid increase in pressure is observed, and a peak pressure is reached within a short period. Then, even if the injection pressure is maintained constant, the mold pressure begins to decrease due to cooling and the consequent increase in the density of the material. The observed reduction of volume is related to the fact that polymer melts are compressible at normal injection pressures.

Spencer and Gilmore (6) developed an approximate equation for the calculation of the maximum pressure in the mold during packing. To achieve this, they combined an equation of state and an empirical equation for the determination of the filling time. The first work considering the packing stage as a transport phenomena problem using the equations of continuity, motion, and energy has been reported by Kamal and Kenig (1) for a semicircular cavity. From this model, temperature and pressure profiles were obtained and compared with experimental data. Later on, Kuo and Kamal (17) extended the theory of Hele-Shaw flow for the analysis of the packing stage associated with a non-Newtonian fluid in a thin, rectangular cavity. They neglected the viscoelasticity and the stress relaxation of the polymer melt.

The approach for the simulation of the packing stage is the same as for the filling stage. Equations of continuity, motion, and energy are simplified using a set of assumptions applicable to the packing stage. A possible set of assumptions is listed below:

- The fluid motion is laminar.
- Body forces are negligible.
- There is no velocity component in the z direction.

For the packing stage, the deceleration motion of the flow reinforces the importance of the unsteady-state terms, and they should not be neglected. It should be pointed out that the convective terms are of a smaller

order of magnitude, relative to the unsteady terms.

The simplified continuity and momentum equations are:

$$\begin{aligned}\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(\rho V_x) + \frac{\partial}{\partial y}(\rho V_y) &= 0 \\ \rho \frac{\partial V_x}{\partial t} &= - \frac{\partial P}{\partial x} - \left[\frac{\partial \tau_{xx}}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} + \frac{\partial \tau_{zx}}{\partial z} \right] \\ \rho \frac{\partial V_y}{\partial t} &= - \frac{\partial P}{\partial y} - \left[\frac{\partial \tau_{xy}}{\partial x} + \frac{\partial \tau_{yy}}{\partial y} + \frac{\partial \tau_{zy}}{\partial z} \right] \\ 0 &= - \frac{\partial P}{\partial z} - \left[\frac{\partial \tau_{xz}}{\partial x} + \frac{\partial \tau_{yz}}{\partial y} + \frac{\partial \tau_{zz}}{\partial z} \right]\end{aligned}\quad (5)$$

In the packing stage, the dominant feature is the compressibility of the polymer melt. To include compressibility effects in the analysis, an equation of state should be used. One of the first, and certainly the most widely used equation of state for polymer systems, is the Spencer-Gilmore equation (18), which is listed in Table 1 along with other empirical equations of state.

Equations of continuity, motion, and energy, coupled with a rheological equation and an equation of state, should be solved simultaneously in order to simulate the packing stage.

Cooling Stage

The freezing of the gate occurs after the filling and the packing of the cavity. During this stage, no additional material enters the cavity, and thus, there is no fluid motion. The problem is reduced to the transient heat transfer by conduction of a polymer melt trapped between two cooling plates. Kamal and Kenig (1) solved this problem for a circular cavity using a one-dimensional heat-conduction equation with variable polymer properties. The heat generated by crystallization is accounted for by using an equivalent temperature. In order to obtain a better representation of the heat transfer

Table 1. Some Empirical Equations of State for Polymers*

Spencer and Gilmore

$$(P + \pi)(\bar{V} - \omega) = RT$$

π = internal pressure

ω = specific volume at 0°C

R = material constant

Breuer and Rehage

$$\bar{V}(T, P) = \bar{V}_0 + \phi_0 T - \frac{K_0}{a} (1 + bT) \ln(1 + aP)$$

a, b = material parameters

$\bar{V}_0$ = the volume at 0°C and zero pressure

ϕ_0 = $(d\bar{V}/dT)_P$ at 0°C and zero pressure

K_0 = $(d\bar{V}/dP)_T$ at 0°C and zero pressure

Kamal and Levan

$$\rho(T, P) = \rho_\infty + \left(\frac{\partial \rho}{\partial P} \right)_{P=0} T + (a + bT)P + \frac{1}{2} (c + dT)P^2$$

ρ_∞ = density at 0°C and zero pressure

a, b, c, d = adjustable material parameters

*see Ref. 8

phenomena accompanied by a change of phase, a recent model developed by Dietz (19) can be used to represent the nonsteady-state heat transfer in the mold. The approach is modified by the addition of a term accounting for the heat generated by the crystallization of the polymer.

$$\frac{\partial T}{\partial t} = \alpha \left[\frac{\partial^2 T}{\partial x^2} + \frac{1}{K} \left\{ \frac{\partial K}{\partial T} \left(\frac{\partial T}{\partial x} \right)^2 + \frac{T}{V} \left(\frac{\partial v}{\partial T} \right) \rho \frac{dP}{dT} \right\} \right] + r \Delta H \quad (6)$$

Each of the terms on the right-hand side of the equation may be given the following interpretation:

- K = thermal conductivity
- ρ = density
- C_p = specific heat at constant pressure
- V = specific volume
- r = rate of crystallization
- H = heat of crystallization
- α = thermal diffusivity

Equation 6 must be solved and coupled with an equation for the rate of crystallization. Different possibilities for a rate equation will be discussed in a subsequent section.

CONSTITUTIVE EQUATIONS

Equations of continuity, motion, and energy are expressed in terms of the stress tensor. In order to use these equations to determine velocity distributions, it is necessary to express the various stresses in terms of velocity gradients and fluid properties. Such a relationship between the stress tensor and some measurement of the deformation is called a "constitutive equation." A very practical and simple rheological equation widely used in engineering is the Newtonian fluid equation:

$$\vec{\tau} = - \mu \vec{\dot{\gamma}} \quad (7)$$

- $\vec{\tau}$ = stress tensor
- $\vec{\dot{\gamma}}$ = rate-of-deformation tensor
- μ = constant for a given T , P , and composition

There is a difficulty in using the above equation for a polymer melt, since the viscosity of a macromolecular fluid depends on the rate of deformation and is therefore not constant. In order to obtain a simple formulation applicable to polymeric systems, rheologists have commonly employed the generalized Newtonian fluid equation:

$$\vec{\tau} = - \eta \vec{\dot{\gamma}} \quad (8)$$

where η is a function of the scalar invariants of $\vec{\dot{\gamma}}$.

Equation 8 has been used by numerous workers in order to model the filling process using a relatively simple rheological equation. However, this model does not properly account for normal forces or for the time-dependent phenomena that are very important for a viscoelastic fluid. If information is desired on the morphology and orientation of the molded part, it is neces-

sary to follow the development and relaxation of shear and normal stresses throughout the various stages of the molding cycle. Thus, a more accurate description of the stress field during processing is essential for the determination of the microstructure of the final article.

Several papers published over the last few years have produced numerical solutions of non-Newtonian flow using either finite-difference or finite-element methods. Crochet and Pilate (20) used a finite-difference method to study the flow of a second-order fluid through three types of plane channels with a contraction. In another work (21), they considered the flow of a second-order fluid past submerged obstacles, such as circular and elliptical cylinders, in order to induce inertia effects. Given the fact that second-order fluids are restricted to very slow flows in which the boundary conditions vary smoothly with time, a more thorough analysis would require the use of an implicit rheological equation. Perera and Walters (22) solved the problem of the flow of a viscoelastic liquid in L-shaped and T-shaped geometries as well as the expansion/contraction/expansion problem. A finite-difference technique was used in conjunction with an implicit rheological equation of the Oldroyd type. A finite-element technique was used by Kawahara and Takeuchi (23) to solve the flow of an incompressible viscoelastic fluid through channels with complicated shapes. A Maxwell-type constitutive equation was used. The same mixed finite-element method was used by Crochet and Bezy (24), with a different constitutive equation developed by Thien and Tanner (25). The flows considered were the hole-pressure error and the die-entry flow in a 2:1 contraction.

Regarding the injection-molding process, only one study is reported in the literature, in which a viscoelastic constitutive equation has been employed. Isayev and Hieber (26) used an idealized one-dimensional injection-molding model to study the influence of the processing variables and mold dimensions upon residual flow-induced stresses and associated birefringence in the molded part. However, they considered only the filling and cooling stages of the process, neglecting the packing stage. A Leonov (27) constitutive equation, which is based upon the thermodynamics of irreversible processes, was used.

The first step in the selection of a constitutive equation is to determine which of the relevant equations, integral or derivative, will be more readily adaptable for a solution using a finite-element or finite-difference technique. The choice of a constitutive equation will be made with consideration to the characteristics of the process. Table 2 gives some of the constitutive equations that can be considered. Also, it is possible that actual data relating to normal stresses and stress relaxation as functions of shear rate and temperature can be employed in the solution.

MICROSTRUCTURE PREDICTION

The modeling approach presented above doesn't only with the hydrodynamic and heat-transfer aspects of the molding process. In this section, we deal with aspects

Table 2. Some Constitutive Equations for Polymer Melts*

Designation	Model
Maxwell	$\dot{\gamma} + \lambda_0 \frac{\partial \dot{\gamma}}{\partial t} = -\eta_0 \dot{\gamma}$
White-Metzner	$\dot{\gamma} + \frac{\eta}{G} \frac{\partial \dot{\gamma}}{\partial t} = -\eta \dot{\gamma}$
4-Constant Oldroyd	$\dot{\gamma} + \lambda_1 \frac{D\dot{\gamma}}{Dt} + 1/2 \mu_0 (\dot{\gamma} \dot{\gamma}) = -\eta_0 \left[\dot{\gamma} + \lambda_2 \frac{D\dot{\gamma}}{Dt} \right]$
Lodge's Rubberlike	$\dot{\gamma} = + \int_{-\infty}^t M(t-t') \dot{\gamma}(t') dt'$
K-KZ Model	$\dot{\gamma} = + \int_{-\infty}^t \left[M_1(t-t', I, II) \dot{\gamma}(t') + M_2(t-t', I, II) \left\{ \dot{\gamma}(t') \cdot \dot{\gamma}(t') \right\} \right] dt'$

*See Ref. 38

relating to the development of microstructure during processing. The main contributions to microstructure arise from the occurrence and development of crystallization and/or orientation in the molded article. Therefore, microstructure-related models should deal with the analysis of the factors influencing these phenomena.

Crystallization

Morphological Zone: According to Tan and Kamal (28), four different morphological zones have been observed in articles obtained by the injection molding of partially crystalline polymers (e.g., high-density polyethylene):

- Zone 1: exhibits a nonspherulitic structure, located near the wall, that has a high degree of orientation in the flow direction.
- Zone 2: also near the wall, is subjected to very large thermal gradients. Thus, the nucleation rate is very fast, and the spherulites are fine and asymmetric.
- Zone 3: consists of asymmetric oblate spherulites, with the axis of symmetry in the direction of the thermal gradient.
- Zone 4: contains randomly nucleated spherulites crystallized under quiescent conditions.

Development of the above zones is related to phenomena occurring during the three stages of the molding process.

According to Tan and Kamal (28), two zones are formed (Zones 1 and 2) during the filling stage. The polymer entering the cavity and striking the mold wall is subjected to a high shear stress in the flow direction, and rapid crystallization occurs at the mold wall. The molecules that freeze under the high shear stress form tiny fibrils in the direction of the flow. These fibrils act as nuclei for the subsequent growth of folded-chain lamellae. The resulting structure is called "row structure," because the oriented lamellae grow from a con-

tinuous series of nuclei along the flow lines. The row-nucleated structure is associated with Zone 1.

After the formation of the skin, the melt adjacent to this region is subjected to large thermal gradients that induce a very fast nucleation rate, thus limiting the size of the spherulites. The shear force acting in this region results in the orientation of the spherulites and the development of Zone 2.

The packing stage is associated with low shear rates and a low nucleation rate. Large spherulites are formed, and growth is in the direction of the thermal gradient. Therefore, oblate spherulites are formed (Zone 3).

During the final cooling stage, the shear stresses have disappeared except for those chains undergoing relaxation, and the thermal gradient is small. Quiescent crystallization can take place, and spherulites are formed and grow until impingement.

Crystallinity: When a polymer crystallizes from the melt, its structure is not perfect. Amorphous material may be observed within and between crystalline entities. Accordingly, to characterize the amount of crystalline material, it is useful to refer to "volume fraction of crystallinity" or "degree of crystallinity," X_C :

$$X_C = \frac{V_A - V}{V_A - V_C} \quad (9)$$

- V = specific volume of the specimen
- V_A = specific volume of the amorphous material
- V_C = specific volume of the pure crystal

In order to study crystallization kinetics, dilatometry, which consists of following the variation of specific volume with time under controlled thermal conditions, may be employed. Equation 9 may be used to convert specific volume measurements to the degree of crystallinity values. Alternatively, crystallization kinetics may be studied isothermally or in the dynamic mode by using differential scanning calorimetry (DSC). Under these conditions, crystallinity is determined by

following the heat of crystallization as a function of time. A relationship similar to Eq 9 converts heat of crystallization measurements to degree of crystallinity values. Typical isothermal crystallization data are shown in Fig. 5.

Kinetics of Crystallization: The spherulitic crystallization process may be divided into three stages: The first stage corresponds to nucleation; the second stage is associated with the growth of the spherulite by the formation of crystalline fibrils with many branches; and the third stage involves crystallization of the intervening regions between the already crystallized fibrils (see Fig. 5). The third stage begins somewhere during the growing process, but it can persist for a long period of time after all spherulites have impinged and ceased to grow.

The growth process (Stage 2) can be represented by the Avrami equation:

$$X(A, t) = X(A, \infty) [1 - \exp(-Zt^n)] \quad (10)$$

where

- $X(t)$, $X(\infty)$ = crystallinity at time t and infinity, respectively
- n = integer depending on the shape of the growing crystallite
- Z = constant depending upon the nucleation and growth rates.

As shown in Fig. 6, the Avrami equation yields good predictions only for low degrees of crystallinity occurring during the early stages of growth, due to the fact that this equation does not take into account secondary crystallization. Stage 3 (Fig. 5) can be visualized as a further crystallization inside the spherulites during and after growth.

Gordon and Hiellier (29) developed an equation, following the rate equation of Hirai and Eyring (30), that can represent the whole curve. The crystalline entities (spherulites) grow in the melt, according to the rate equation of Avrami, and a volume element is incorporated in the growing entity to represent the further crystallization. This volume element can continue to crystallize after the growing entity has reached its final

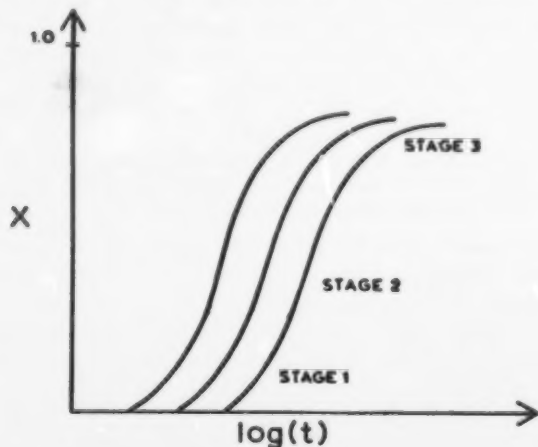


Fig. 5. Crystallization kinetics.

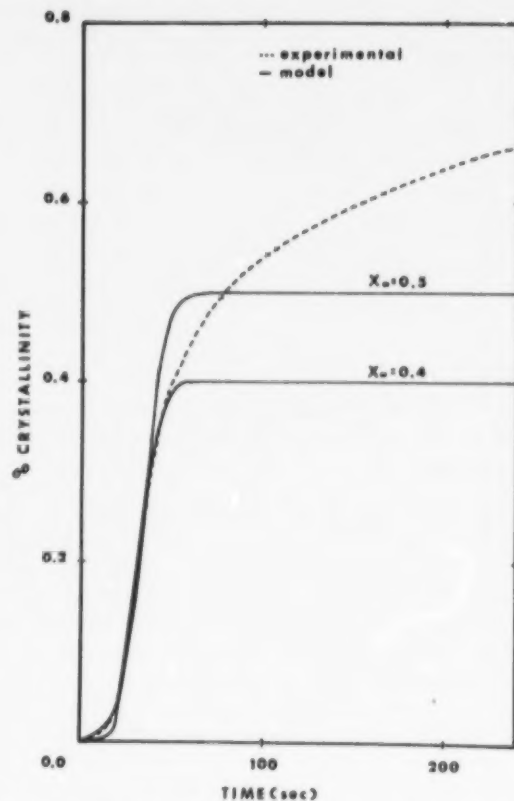


Fig. 6. Kinetics of isothermal crystallization, Avrami model.

crystallinity (secondary crystallization). The proposed equation takes the following form:

$$X(C, t) = X(A, \infty) [1 - \exp(-Z_1 t^n)] + X(S, \infty) Z_2 \int_0^t [1 - \exp(-Z_1 \theta^n) \exp(-Z_2 (t - \theta))] d\theta \quad (11)$$

$X(A, \infty)$, Z_1 , n = final degree of crystallinity, rate constant, and exponent of the primary spherulitic growth.

$X(S, \infty)$, Z_2 = final increased degree of crystallinity and the first order rate constant of the secondary process.

The four parameters, $X(A, \infty)$, $X(S, \infty)$, Z_1 , and Z_2 , can be determined by a fitting of Eq 11 using the experimental crystallization isotherm. However, a recent study (31) shows that the parameters $X(A, \infty)$, $X(S, \infty)$, and Z_1 can be determined by using the Avrami crystallization isotherm. Thus, the only parameter that has to be fitted is Z_2 . Figure 7 shows that good agreement is obtained by employing Eq 10 in conjunction with the Avrami parameters calculated from the primary crystallization part of the isotherm.

The equation of Avrami and the modified one of Gordon and Hiellier have been developed for isothermal crystallization. The different parameters $X(A, \infty)$, $X(S, \infty)$, Z_1 , and Z_2 are all functions of temperature. In the molding process, it is obvious that the crystalliza-

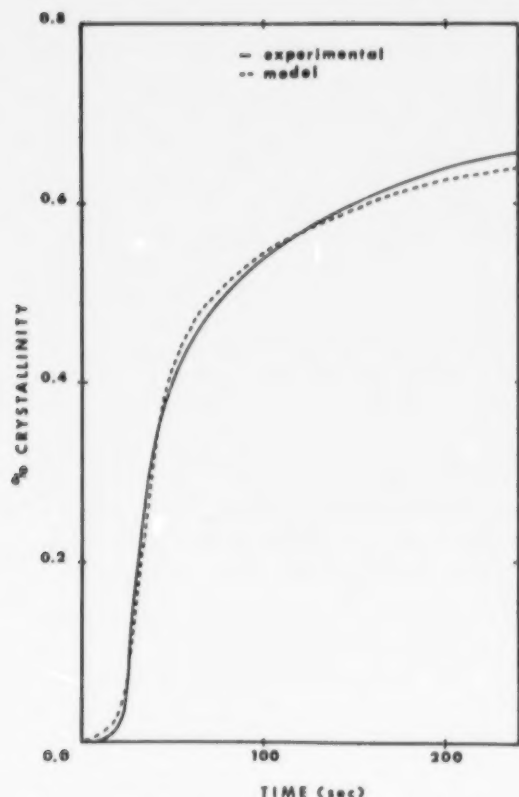


Fig. 7. Kinetics of isothermal crystallization, modified Avrami model.

tion is nonisothermal; for this reason, Nakamura, *et al.* (32), derived a modified Avrami equation for a nonisothermal process:

$$X(t) = 1 - \text{Exp} \left[- \left\{ \int_0^t K' [T(\tau)] d\tau \right\}^n \right] \quad (12)$$

where n is the Avrami index determined from isothermal experiments, $K'(T)$ is connected with the crystallization rate constant of isothermal crystallization, $K(T)$, through the relation

$$K'(T) = [K(T)]^{1/n} \quad (13)$$

Using this equation, the crystallinity-time relation in a nonisothermal process can be predicted from isothermal crystallization data (Chu and Kamal (31)).

Orientation

The thermomechanical history of the melt during processing is responsible for the orientation of the polymer chains, causing frozen stresses and the nonuniform morphology of the semicrystalline molded article. In the previous section on crystallization, we defined four different morphological zones formed under different levels of stress during the process. Orientation, which is also associated with frozen stresses, may be estimated by measuring birefringence of the sample. Birefringence is the measure of the difference in the refractive index of the stretched sample in the directions parallel and perpendicular to stretching. Other techniques to

determine orientation involve wide-angle x-ray diffraction, infrared dichroic ratio, sonic speed, etc.

Some studies have been carried out in order to relate the stress field during processing to the orientation (birefringence) of a thermoplastic polymer, but these studies are generally related to amorphous polymers in order to avoid the complication of combined amorphous and crystalline orientation functions. Oda, White, and Clark (33) reported in an experimental study on polystyrene melts that the orientation in vitrified polystyrenes can be predicted by a knowledge of the stress field prior to solidification and application of stress-optical laws, where the birefringence can be related to the stress field through the stress optical coefficient. Similar results have been reported by Kamal and Tan (34) on a polystyrene melt using a relation developed by Wales (35) to relate the birefringence to the shear stress at the wall. In the work of Isayev and coworkers (36), the relationship between stress and birefringence is used in the case of the injection of an amorphous polymer. Thus, the stress field is determined using a viscoelastic equation, and the birefringence is calculated.

When semicrystalline polymers are employed, birefringence of the melt prior to solidification and birefringence of the crystalline product are not the same. A possible approach would be to consider a combination of the two phenomena: orientation of the melt and orientation during the crystallization process.

NUMERICAL METHODS

The resulting dynamic problem, consisting of the continuity equation, the energy equation, the dynamic equations, and the set of associated constitutive (rheological and thermal) and thermodynamic relationships, forms a system of multiple, simultaneous, coupled, nonlinear, partial differential equations that can only be solved by a numerical technique. In the particular case of the filling stage, a free surface, due to the transient nature of the operation, is involved.

When the transient and inertial terms are neglected, it is possible to employ an inexpensive, explicit, finite difference scheme (1, 9, 11). For regular wall boundaries (eg., disk or rectangular cavities), it is possible to use a finite-difference method like the Marker-and-Cell (M.A.C.) technique, which is suitable for treating free surface and transient flow (37). However, when the unsteady-state terms of the momentum equations are included, it is necessary to use implicit finite-difference equations because of the restriction on the time step, due to the extremely low Reynolds number. In this case, the finite-difference implicit solution can be as expensive as a finite element solution, which has the advantage of being more flexible regarding the shape of the studied domain (36).

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Discussion on M. R. Kamal Articles

L. A. Utracki. I have two questions. Firstly, a question regarding the predictability of the morphology. What method or model did you use to predict the morphology? Are you predicting this from the intrinsic birefringence of the molded specimens or from fundamental

properties of the resin and the molding parameters? The second question relates to the observation that, in your graphs, the predicted curves indicated shorter filling time than experimental results. Is it possible that this discrepancy is due to the omission of elongational effects in your calculations?

M. R. Kamal. With regard to the question about crystallinity and morphology, the approach that we have taken is that it is necessary to predict the distributions of crystallinity and orientation functions (amorphous and crystalline) for a useful description of the system. In order to achieve this, the computer simulation must incorporate appropriate crystallization kinetics models and suitable constitutive equations that permit the estimation of the distributions of both crystallinity and orientation functions. Professor Wang and coworkers at Cornell University have already established the feasibility of predicting some mechanical properties of polystyrene (amorphous) moldings by utilizing a suitable constitutive equation. The treatment of partially crystalline polymers is more complex, but it should also be feasible.

With regard to the elongational viscosity effect, the total model must incorporate viscoelastic phenomena and must take into account the elongational phenomena, especially near the melt front. However, it has been shown that neglecting elastic effects does not lead to serious error in predicting filling times and the position of the melt front, in most practical cases. Viscoelastic effects do become important during later stages and play an important part in determining the ultimate microstructure of the molded article. Therefore, they should be incorporated in a model aimed at predicting microstructure. A suitable constitutive equation should yield good predictions of normal stress distributions and the relaxation behavior of the material.

B. Favis. You have indicated the need to extend the models in order to deal with more complex molds. How about the need to deal with more complex materials; for example, blends and reinforced systems?

M. R. Kamal. Generally, commercial resins, whether based on one polymer, a polymer blend, or a reinforced system, are molded in cavities that are far more complex than the circular or rectangular cavities considered in most modeling studies. In my view, the extension of molding work to cope with such complex cavities will yield the highest return from the commercial point of view. On the other hand, the question of dealing with polymer blends or fiber-reinforced polymers relates mainly to the establishment of the appropriate models for the material itself; i.e., the identification of appropriate constitutive equations and other relationships describing material behavior. The process simulation for simple cavities will be similar to that described in my presentation for simple materials.

Mathematical Modeling of the Blow-Molding Process

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A mathematical simulation of the blow-molding cycle has been developed by combining general conservation principles along with appropriate constitutive relations for the material. A model of the parison formation stage has been devised by considering the competing effects due to swell and drawdown. A more rigorous numerical analysis of parison formation is also discussed. A theoretical treatment of parison inflation is described for both inelastic and viscoelastic materials by assuming uniform radial growth. Comparisons are made with experimental data for all phases of the molding cycle. The mathematical model is in reasonable quantitative agreement with experimental results and is capable of elucidating the influence of material properties and process conditions on the dynamics and performance of the blow-molding process.

INTRODUCTION

Although the first attempts to blow mold hollow plastic articles were undertaken by John Wesley Hyatt about a century ago by introducing steam between two sheets of cellulose nitrate clamped within a mold, large-scale development did not occur until the early 1950s. Large-volume applications were primarily the result of the availability of low-cost polyolefin materials and the increased demand for packaging applications subsequent to World War II.

Blow molding is now a commercially important polymer processing operation used for the production of hollow articles and containers. The continued popularity and importance of this process is evident from the enormous growth and diversification of the plastics container industry in recent years. Exploratory studies aimed at developing a fundamental scientific understanding of the process are relatively recent. For convenience in description and analysis, the entire blow-molding cycle may be considered as consisting of a sequence of related steps. These sequential steps are depicted schematically in Fig. 1. Initially, a parison of the requisite length is formed by extruding the molten polymer through an annular die. This hollow cylindrical parison is then inflated within the mold in order for the polymer to assume the shape or contour of the cavity. The polymer is solidified and ejected from the mold in order to complete the cycle.

MATHEMATICAL SIMULATION OF THE PROCESS

A mathematical model of each of the stages comprising the blow-molding cycle is subsequently described by considering the appropriate constitutive relations and conservation principles that apply to the various steps in the process.

Parison Formation

The process of parison formation constitutes a formidable non-Newtonian fluid mechanics problem, consisting of the unsteady, nonisothermal, free-surface flow of a viscoelastic material from an annular die. A rigorous analysis of parison formation may be developed by means of a direct numerical solution of the governing equations of change. Several studies have been undertaken relating to the steady "extrudate swell" or "jet swell" problem using a finite-element numerical method (1-13). Recently, a numerical scheme based on a traditional finite-difference formulation has been suggested for the solution of steady, free-surface flow problems (14, 15). This technique is based upon a stream function-vorticity formulation and has been successfully applied to the jet swell of Newtonian fluids in circular and annular geometries. The essence of the method involves the transformation of the irregular flow domain into a uniform rectangular region. However, the application of either a finite-element or finite-difference scheme to the inherently unsteady problem of parison formation of a viscoelastic fluid has not yet been undertaken.

The final shape of the parison is essentially determined by the competing influences due to gravitational forces and elasticity. A simple mathematical simulation of parison formation may therefore be devised by developing a separate quantitative description of the drawdown and swell phenomena.

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Fig. 1. Schematic representation of the extrusion blow-molding cycle.

For the majority of industrial blow-molding dies, the ratio of the outer to inner radius is typically less than three, and thus, curvature effects associated with the annular geometry may be neglected (16, 17). Application of the principle of conservation of mass therefore yields

$$L_s(t) = \frac{V_E \cdot t}{S_D} \quad (1)$$

where $L_s(t)$ denotes the parison length as a function of time subject only to swell, V_E is the extrusion velocity, t is time, and S_D is the swell ratio. Thus, the parison length, subject only to swell, is less than the length corresponding to ideal extrusion and can only be ascertained from a knowledge of the swell ratio, S_D . From experimental data, the time-dependent swell in the absence of gravitational effects may be represented as follows:

$$S_D = 1 + (S_{DEQ} - 1)(1 - \exp(-k_1 t)) \quad (2)$$

where S_{DEQ} is the equilibrium swell ratio and k_1 is a rate constant. These two quantities may be readily determined experimentally (17).

An estimate of the influence of gravitational forces on the length and shape of the parison may be obtained by assuming that the axial velocity is of the form $v_x = v_x(x, t)$ and that the process is isothermal. A schematic representation of the flow situation is shown in Fig. 2. The requirement that both the shear and normal stresses must vanish along the free surface gives

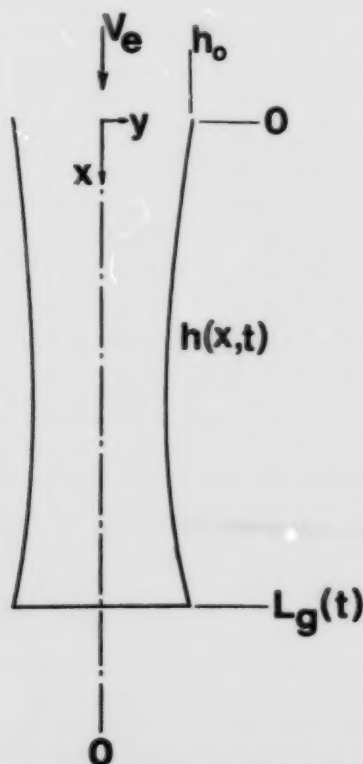


Fig. 2. Schematic representation of parison subject only to drawdown.

$$T_{yy}n_y + T_{xy}n_x = 0 \quad (3)$$

$$T_{xy}n_y + T_{xx}n_x = 0 \quad (4)$$

where T_{ij} denotes the total stress component and n_x and n_y are the components of the unit vector normal to the free surface and are given by:

$$n_x = -\frac{\partial h}{\partial x} \left(1 + \left(\frac{\partial h}{\partial x} \right)^2 \right)^{-\frac{1}{2}} \quad (5a)$$

$$n_y = \left(1 + \left(\frac{\partial h}{\partial x} \right)^2 \right)^{-\frac{1}{2}} \quad (5b)$$

Rearrangement of Eqs 3 and 4 and making use of Eq 5 gives:

$$T_{xy} = T_{xx} \frac{\partial h}{\partial x} \quad (6a)$$

$$T_{yy} = T_{xx} \left(\frac{\partial h}{\partial x} \right)^2 \quad (6b)$$

Integrating the equation of motion in the x direction with respect to y from the centerline ($y=0$) to the free surface ($y=h$), and making use of Eq 6, gives:

$$\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} = \frac{1}{\rho} \frac{\partial T_{xx}}{\partial x} + \frac{T_{xx}}{\rho h} \frac{\partial h}{\partial x} + g_x \quad (7)$$

The deviatoric stress, τ_{ij} , is related to the total stress, T_{ij} , as follows:

$$T_{ij} = -P \delta_{ij} + \tau_{ij} \quad (8)$$

where

$$P = -\frac{1}{3} T_{ii} \quad (9)$$

The repeated subscript implies the adoption of the index summation convention. Assuming that the surface curvature is reasonably small ($\partial h / \partial x \ll 1$) implies that $T_{yy} \approx 0$. Since $T_{zz} = 0$, Eqs 8 and 9 imply that $T_{xx} = 3/2 \tau_{xx}$. Therefore, Eq 7 becomes

$$\frac{\partial v_x}{\partial t} + v_x \frac{\partial v_x}{\partial x} = \frac{3}{2\rho} \frac{\partial \tau_{xx}}{\partial x} + \frac{3\tau_{xx}}{2\rho h} \frac{\partial h}{\partial x} + g_x \quad (10)$$

In addition, the movement of the free surface is governed by the following kinematic condition:

$$\frac{\partial h}{\partial t} = v_y - v_x \frac{\partial h}{\partial x} \quad (11)$$

Integration of the continuity equation with respect to y yields:

$$v_y = -y \frac{\partial v_x}{\partial x} \quad (12)$$

Substitution of this result applied at the free surface into Eq 11 gives:

$$\frac{\partial h}{\partial t} + \frac{\partial}{\partial x} (h v_x) = 0 \quad (13)$$

The following identity may also be written:

$$\frac{dL_g}{dt} = v_x(L_g, t) \quad (14)$$

Equations 10, 13 and 14, along with an appropriate constitutive equation relating the deviatoric stress tensor, $\underline{\tau}$, to the rate of deformation tensor, $\underline{\Delta}$, provide the mathematical description for the drawdown analysis. These governing equations constitute a set of coupled, nonlinear, partial differential equations. In addition, a further complication arises from the fact that the flow domain (L_g, h) is not known *a priori* but must be determined as part of the solution. Simple analytical solutions to the above system of partial differential equations may be obtained by making additional assumptions with regard to the kinematics of the deformation (17, 18). For example, if the convective terms in the equation of motion are neglected and the surface profile is considered to be independent of axial location, integration of Eq 10 yields

$$\tau_{xx} = \frac{2}{3} \rho g_x (L_g - x) \quad (15)$$

Further, if the fluid is assumed to be described by means of a corotational Maxwell model, then:

$$\tau_{xx} + v_x \lambda_o \frac{\partial \tau_{xx}}{\partial x} = 2 \eta_o \frac{\partial v_x}{\partial x} \quad (16)$$

where λ_o and η_o are rheological parameters. Substitution of Eq 15 into Eq 16 and solving for the axial velocity subject to the condition that $v_x(0, t) = V_E$ gives

$$v_x = V_E \exp(-\alpha \lambda_o x) + \frac{L_g}{\lambda_o} (1 - \exp(-\alpha \lambda_o x)) - \frac{1}{\alpha \lambda_o^2} (\alpha \lambda_o x + \exp(-\alpha \lambda_o x) - 1) \quad (17)$$

where $\alpha = \rho g_x / 3 \eta_o$. Making use of Eq 17 in Eq 14 enables a relationship between parison length and time to be derived as follows

$$t = \int_0^{L_g} \frac{dL}{\frac{(1 - \exp(-\alpha \lambda_o L))}{\alpha \lambda_o^2} + \left(V_E - \frac{L}{\lambda_o}\right) \exp(-\alpha \lambda_o L)} \quad (18)$$

The expressions for the length contributions due to swell and gravity may be combined in order to yield the resulting parison shape subject to these two competing influences. Figure 3 shows the calculated variation of the functions L_s and L_g with time. By adding the difference between pure drawdown and ideal behavior to the swell contribution, the actual parison length may be calculated as a function of time. A comparison is made with experimental data obtained using a commercial blow-molding grade, high-density polyethylene resin (Phillips Petroleum Co., Marlex EHM-6006). Parameter values and material properties are summarized in Table 1. Although the theoretical model provides some useful insight on the influence of material properties and process parameters on the parison formation stage, it is evident that the model fails to accurately describe

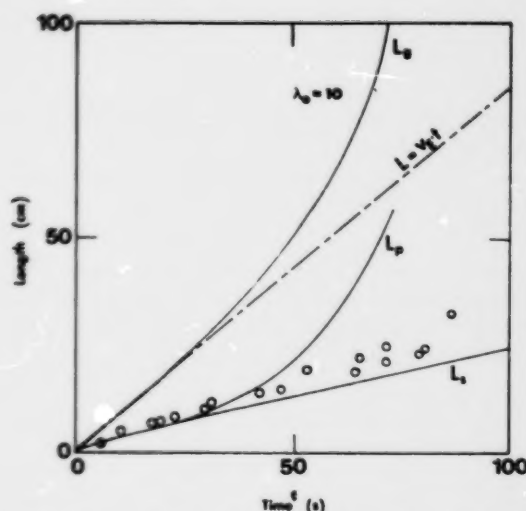


Fig. 3. Calculated and experimentally determined parison length as a function of time.

the growth of the parison, particularly at longer times. This failure may be due to several possible causes, including the unrealistic nature of many of the simplifying assumptions in the preceding analysis, the choice of constitutive equation for representing the rheological response of the material, inaccuracies associated with material characterization, and the assumed simple additivity of the contributions due to swell and drawdown.

Parison Inflation

Although parison inflation plays a significant role in determining the quality of a blow-molded product, very few studies have been undertaken relating to this aspect of the molding cycle. Simple analyses involving the inflation of a power-law liquid may be found in the texts of Middleman (19) and Tadmor and Gogos (20). The simultaneous inflation and extension of a viscoelastic tube has been analyzed by Coleman (21), Foster and Shaffers (22), Chung and Stevenson (23), and Wineman (24).

A mathematical model of the inflation process may be derived by considering the radial growth of a thin, cylindrical tube subjected to a constant internal pressure. This idealized situation neglects end effects associated with either the die or the clamping mechanism. The process is also considered to be isothermal. The continuity equation and the radial component of the equation of motion may therefore be expressed as follows:

$$\frac{\partial}{\partial r} (rv_r) = 0 \quad (19)$$

Table 1. Parameter Values and Material Properties

$S_{D\tau Q}$	= 1.92
V_E	= 0.86 cm/s
k_1	= 0.09684 s ⁻¹
η_o	= 3800 Pa·s (3.8 · 10 ⁴ poise)
λ_o	= 10 s
ρ	= 964 kg/m ³

$$\rho \left(\frac{\partial v_r}{\partial t} + v_r \frac{\partial v_r}{\partial r} \right) = - \frac{\partial P}{\partial r} + \frac{\partial \tau_{rr}}{\partial r} + \frac{\tau_{\theta\theta} - \tau_{\phi\phi}}{r} \quad (20)$$

Since $v_r(R, t) = dR/dt = \dot{R}$, integration of Eq 19 gives the radial velocity as

$$v_r = \frac{R \dot{R}}{r} \quad (21)$$

where R denotes the internal parison radius. The boundary conditions at the internal ($r=R$) and external ($r=S$) surfaces are given by the following force balances:

$$r=R \quad P - \tau_{rr} + \frac{\sigma}{R} = P_i \quad (22a)$$

$$r=S \quad P - \tau_{rr} - \frac{\sigma}{S} = P_o \quad (22b)$$

where P_i is the internal inflation pressure, P_o is the external air pressure, and σ is the surface tension of the fluid. $\Delta P = P_i - P_o$ is the driving force for inflation. Equation 20 may be integrated from $r=R$ to $r=S$ with the aid of Eqs 21 and 22. Assuming that the parison thickness, $\delta = S - R$, is much smaller than the radius, ($\delta/R \ll 1$), the integrated equation becomes:

$$\Delta P - \frac{\sigma}{R} \left(2 - \frac{\delta}{R} \right) - \rho \ddot{R} \delta = - \int_R^S \frac{\tau_{rr} - \tau_{\theta\theta}}{r} dr \quad (23)$$

Equation 23 is the general expression describing the growth of a cylindrical parison subject to an applied pressure difference, ΔP .

The growth profile may be determined by combining an appropriate viscoelastic constitutive equation with Eq 23. The resulting nonlinear integro-differential equation is not amenable to simple analytical solution except in some limiting special cases. For the case of a rate-type constitutive equation, the governing growth equation has the form of an initial-value problem and may be solved by means of a fourth-order Milne predictor-corrector technique. This approach has been used for the case of a modified Zaremba-Fromm-DeWitt model, suggested by Pearson and Middleman (25), as well as for a modified White-Metzner fluid (26). The details of the analysis and computational procedure are provided elsewhere (27, 28).

Figure 4 and 5 illustrate the growth behavior for these two rheological models. During the initial stages of the process, faster inflation is associated with greater elasticity of the material. However, at longer times, the viscoelastic growth rate gradually decreases below the corresponding Newtonian case. Similar results have been reported by Bird, *et al.* (29), for the expansion of a spherical viscoelastic shell described by an Oldroyd "fluid B" model. Failure of the numerical method ultimately occurred at some time level for all nonzero values of Deborah number. Similar computational difficulties have been reported by Wineman (24).

Once the melt has contacted some part of the mold surface, the deformation becomes restricted in certain

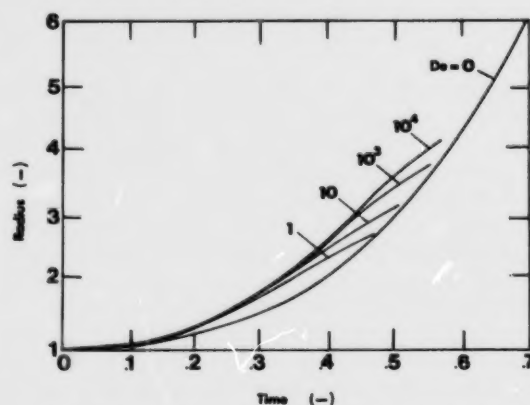


Fig. 4. Inflation behavior for a modified Zaremba-Fromm-DeWitt fluid.

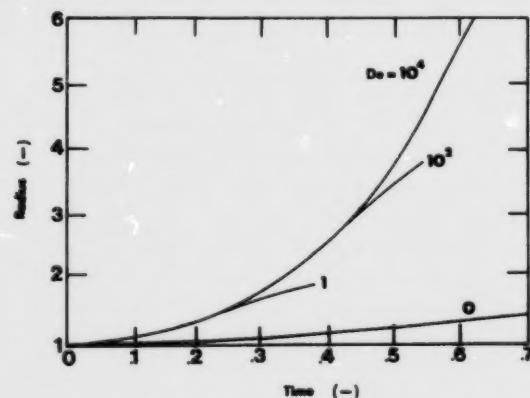


Fig. 5. Inflation behavior for a modified White-Metzner fluid.

directions. This phase of the inflation process is termed "confined" inflation. Since this constitutes the final shape-forming step in the blow-molding process, confined inflation plays an important role in determining the ultimate shape and wall-thickness distribution of the molded product. Only a few relevant investigations pertaining to this facet of the molding cycle have appeared in the literature. Petrie (30) has presented a simple analysis for determining the thickness variation of a cylindrical parison inflating within a mold having a square or rectangular cross-section. A similar study has been made by Fukase, *et al.* (31). They formulated expressions for the thickness changes associated with various geometrical forms. Recently, Vul'f, *et al.* (32), and Rosenzweig, *et al.* (33), have reported similar analyses in relation to the thickness variations accompanying the vacuum-forming and thermoforming processes, respectively.

A mathematical analysis of confined, inflation entails the specification of the following assumptions:

- The deformation is isotropic.
- The parison possesses uniform thickness at the end of free inflation.
- Inflation occurs isothermally.
- The polymer melt is incompressible.
- The polymer melt solidifies instantaneously upon contact with the mold surface and does not deform further.

A schematic diagram of the molten polymer inflating into a two-dimensional square corner is shown in Fig. 6. At some time, t , the parison (QQ') possesses a uniform thickness, δ , whereas, at some later time, $t + dt$, the parison (MM') has a uniform thickness, given by $\delta - d\delta$. Assuming that the material that has contacted the mold surface within the time interval dt possesses an average thickness of $\delta - d\delta/2$, an elementary material balance yields:

$$\frac{\pi}{2} R\delta = \frac{\pi}{2} (R - dR)(\delta - d\delta) + 2 dR\left(\delta - \frac{d\delta}{2}\right) \quad (24)$$

where R and $R - dR$ denote the radii of the surfaces QQ' and MM' , respectively. Neglecting second and higher-order differential terms gives:

$$\frac{d\delta}{\delta} = \left(\frac{4 - \pi}{\pi}\right) \frac{dR}{R} \quad (25)$$

Integrating Eq 25 from the onset of confined inflation yields:

$$\frac{\delta}{\delta_f} = \left(\frac{R}{R_f}\right)^{0.273} \quad (26)$$

where R_f and δ_f denote the parison radius and thickness at the end of free inflation. Thus, Eq 26 gives the parison wall thickness as a function of shape. Analytical expressions for other geometrical configurations may be similarly derived. For the case of a spherical segment inflating into a three-dimensional orthogonal corner, a similar analysis yields:

$$\frac{\delta}{\delta_f} = \frac{R}{R_f} \quad (27)$$

An estimate of the time required to produce a given shape may be obtained by assuming that the fluid behaves as a power-law liquid. Neglecting surface tension and inertia, a simple force balance between the inflation pressure and the hoop stress may be written as follows:

$$\Delta P = -4K(2)^{n-1} \left(\frac{1}{\delta} \frac{d\delta}{dt}\right)^n \quad (28)$$

where K is the consistency index, n is the power-law index, and $-d(\ln\delta)/dt$ is the extension rate. Rearrang-

ing and integrating Eq 28 from the end of free inflation ($t = t_f$) gives:

$$\ln\left(\frac{\delta}{\delta_f}\right) = -\left(\frac{\Delta P}{2^{n+1}K}\right)^{1/n} (t - t_f) \quad (29)$$

For all practical configurations:

$$\ln\left(\frac{\delta}{\delta_f}\right) = A_c \ln\left(\frac{R}{R_f}\right) \quad (30)$$

where A_c is a geometrical constant. Equation 29 may therefore be combined with Eq 30 in order to give the required inflation time directly as a function of parison shape. Thus,

$$t - t_f = A_c \left(\frac{k \cdot 2^{n+1}}{\Delta P}\right) \ln\left(\frac{R_f}{R}\right) \quad (31)$$

As might be expected, a decrease in the power-law index facilitates inflation.

Figure 7 shows a typical comparison between the calculated wall thickness distribution and experimentally-measured values for the high-density polyethylene (Phillips Petroleum Co., Marlex EHM-6006) considered previously. In general, the results exhibit good qualitative agreement but somewhat poor quantitative agreement. The experimentally-measured maximum thickness exhibits an asymmetry around the square mold cavity, with the largest value occurring at the parting line of the mold. A similar asymmetry associated with the parting line is also observed in symmetrical cylindrical mold cavities. Similar observations have also been reported by Kamal, *et al.* (34). These differences

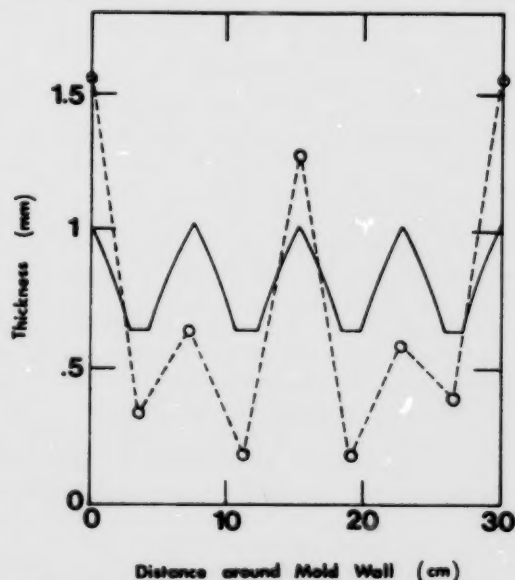


Fig. 7. Comparison of calculated and experimentally determined wall-thickness distribution for a part with square cross-section.

--- Measured
— Calculated
Line pressure = 34.5 kPa (5 psig)
Die temperature = 180°C
 $\delta_f = 1.02475$ mm

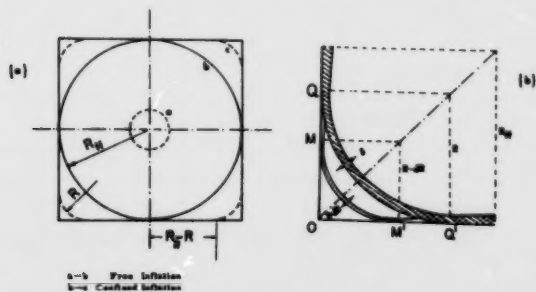


Fig. 6. Schematic representation of inflation into a two-dimensional square corner.

may be due to end effects associated with clamping or to nonisothermal considerations. Despite the poor quantitative agreement, the preliminary theoretical results are encouraging and provide reasonable predictive capability with regard to the effects of material properties and process conditions on the confined inflation behavior.

Heat Transfer

The cooling and solidification of the polymer comprises the major portion of the overall cycle. A mathematical model of the cooling step may be developed by considering the process as an unsteady, one-dimensional heat conduction problem accompanied by a change of phase. Such problems have been treated extensively in the literature (35-40). For polymeric materials, the physical properties are strongly temperature-dependent, especially within the melting range of the material. This necessitates careful consideration of the temperature dependence for the case of heat transfer calculations involving semicrystalline polymers and thereby requires the use of a numerical technique. Heat transfer analyses of the blow-molding process have been given by Dietz (41) and by Edwards, *et al.* (42). Latent heat effects have been included in these analyses by defining an effective specific heat over the melting range of the polymer.

The governing heat conduction equations in the mold and polymer may be expressed as follows:

$$\text{Mold: } \frac{\partial T}{\partial t} = \alpha_m \left(\frac{\partial^2 T}{\partial x^2} + \frac{a}{x} \frac{\partial T}{\partial x} \right) \quad (32)$$

$$\text{Polymer: } \frac{\partial T}{\partial t} = \alpha_p \left(\frac{\partial^2 T}{\partial x^2} + \frac{1}{k} \frac{\partial k}{\partial x} \frac{\partial T}{\partial x} + \frac{a}{x} \frac{\partial T}{\partial x} \right) \quad (33)$$

These equations are applicable to both planar and cylindrical geometries, depending upon the value of the geometry indicator, a ($a=0$ corresponds to a planar configuration, whereas $a=1$ corresponds to a cylindrical configuration). The boundary conditions that apply to this composite-body problem are continuity of temperature and heat flux at the mold-polymer interface and convective flux conditions at the external polymer and mold surfaces. Initially, the polymer and mold temperatures are assumed to be uniform but different in the respective materials. An explicit finite-difference numerical scheme may be used in order to solve the coupled system of equations. Additional information regarding the specification of the boundary conditions and computational procedure is provided elsewhere (27, 43).

The time-temperature history of a high-density polyethylene resin (Phillips Petroleum Co., Marlex EHM-6006) was measured experimentally by means of floating thermocouples (chromel-constantan, 5 mm diameter) embedded in the parison. The precise location of the thermocouples was determined with the aid of a travelling microscope. Figure 8 shows the variation of specific heat with temperature, as determined using a Perkin-Elmer Differential Scanning Calorimeter

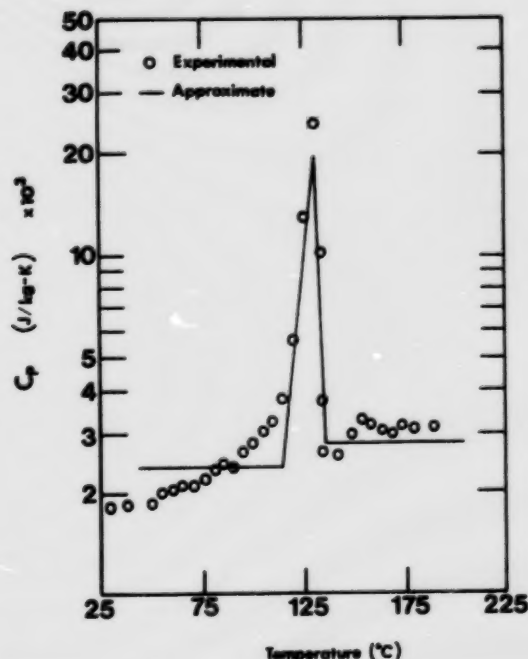


Fig. 8. Variation of specific heat with temperature.

(Model DSC-1b). For calculational purposes, the specific heat variation was approximated by means of a piece-wise linear function, as shown in Fig 8. Figure 9 shows a typical comparison between the experimental and calculated results. The lack of better agreement can probably be attributed to the uncertainty in the thermocouple location and the finite size of the thermocouple bead. A comparison of the present theoretical heat transfer analysis with the experimental and calculated results of Dietz (41) is shown in Fig. 10. Excellent agreement is obtained in this case. The slight hump or plateau (also evident in the experimental data) is due to the latent heat effect.

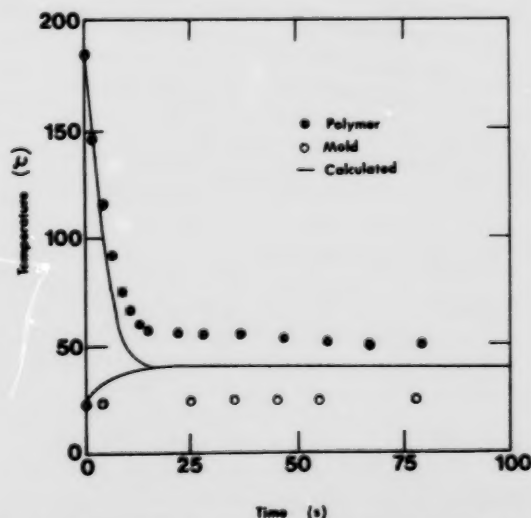


Fig. 9. Comparison of calculated and experimentally determined time-temperature history.

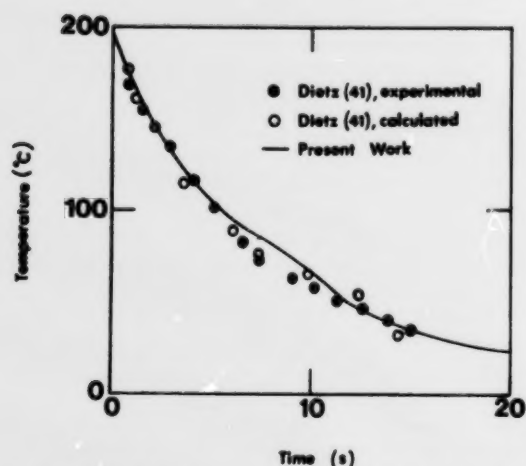


Fig. 10. Comparison of numerical results with the work of Dietz (41).

CONCLUSIONS

A mathematical model of the extrusion blow-molding cycle has been described, including the processes of parison formation, inflation, and solidification. A summary of the conservation principles and constitutive relations that have been employed for each stage of the cycle is given in Table 2.

A simple modeling approach for the analysis of parison extrusion has been developed based upon a mathematical description of parison shape and length due to the competing influences of swell and drawdown. The pure swell behavior is readily modeled by means of an empirical expression and experimentally determined parameters. A one-dimensional formulation allowing for arbitrary surface shape has been suggested for the determination of the length due to drawdown only. An analytical solution of the governing equations is derived by means of several simplifying approximations. The mathematical model exhibits the correct qualitative influence of material properties and process conditions on parison length. The quantitative agreement using the simplified analysis is poor at longer times. Nevertheless, the basic mathematical formulation should provide a realistic foundation for the development of an accurate quantitative analysis.

A generalized analysis has been developed in order to describe the inflation behavior of a viscoelastic material. The elasticity of the material enhances the rate of inflation during the initial phase of expansion. The

thickness distribution associated with confined inflation can be adequately predicted from simple geometrical considerations and mass conservation principles. An estimate of the requisite confined inflation time can be readily estimated by means of a force balance for a power-law fluid. Experimental measurements of the wall thickness variation are in reasonable agreement with the theoretical predictions. Deviations may be the result of asymmetries associated with end effects caused by clamping or the result of nonisothermal conditions.

The cooling of a blow-molded part can be accurately modeled by means of an unsteady, one-dimensional, composite heat conduction analysis involving variable physical properties and a change of phase. Good agreement is obtained between the theoretical calculations and experimental measurements.

The mathematical model described here may serve as a preliminary basis for the development of an understanding of the interaction between material properties, process conditions, and part properties and should permit the formulation and evolution of an accurate, unified mathematical simulation of the entire blow-molding process.

NOMENCLATURE

a	= geometry indicator
A_c	= geometrical constant
g_x	= gravitational force
h	= parison thickness
k	= thermal conductivity
k_1	= rate constant
K	= consistency index for power-law model
L	= parison length
L_D	= parison length due to drawdown effects only
L_S	= parison length due to swell effects only
n	= power-law index
n_x, n_y	= components of unit normal vector at free surface
P	= pressure
P_i	= pressure at internal parison surface
P_o	= pressure at external parison surface
r	= radial coordinate
R	= internal parison radius
$\dot{R}$	= dR/dt
$\ddot{R}$	= d^2R/dt^2
R_f	= parison radius at the end of free inflation
S	= external parison radius
S_D	= swell ratio

Table 2. Mathematical Simulation of the Blow-Molding Cycle.

Stage	Governing conservation equations	Constitutive relations	Solution scheme	References
Parison formation	Continuity, motion	Corotational Maxwell model	Analytical	17, 18
Parison-free inflation	Continuity, motion	Modified ZFD Modified White-Metzner model	Numerical integration	19-24, 27, 28
Parison-confined inflation	Continuity	Power-law model	Analytical	30-34
Cooling and solidification	Energy	—	Finite-difference	35-43

S_{Deq}	= equilibrium swell ratio
t	= time
t_f	= time at the end of free inflation
T	= temperature
T_{ij}	= total stress tensor component
v_r	= radial velocity component
v_z	= axial velocity component
V_E	= extrusion velocity
x, y	= spatial coordinates
α	= $\rho g_x / 3 \eta_0$
α_m	= thermal diffusivity of mold
α_p	= thermal diffusivity of polymer
δ	= parison wall thickness
δ_f	= parison wall thickness at the end of free inflation
δ_{ij}	= Kronecker delta
$\underline{\Delta}$	= rate of deformation tensor
ΔP	= inflation pressure, $P_i - P_o$
η_0	= rheological parameter
λ_0	= rheological parameter
π	= geometrical constant
ρ	= density
σ	= surface tension
τ_{ij}	= deviatoric stress tensor component

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Discussion on M. E. Ryan Paper

Ch. I. Chung. Your assumption of fully-developed flow through the annular part of the blow-molding die is commonly employed. Modern blow-molding practice with parison programming and tapered dies makes this assumption unrealistic. Moreover, most blow-molding resins are very elastic, high-molecular-weight materials with long relaxation times. Thus, the properties of the material change substantially during the process. It also seems that your mathematical analysis of the Newtonian system has no bearing on the final empirical modeling of parison swell where you used the exponential function, thus implicitly including the effects of elasticity and relaxation. Obviously, one cannot neglect elasticity in the treatment of parison behavior. My last comment refers to the stretch of the parison. Many industrial processes nowadays are very fast. To be realistic, one has to include the acceleration force. I do not think that you have done this.

M. E. Ryan. There may have been some confusion with regard to various approaches to deal with the swell problem. My intent was to illustrate two different approaches to understand the development of the parison. One is the rigorous approach, solving in their entirety the governing equations of change, using some sort of numerical scheme. That has progressed to the point that we can handle pretty well the steady-state isothermal Newtonian flow problem. Independent of that is a different approach, trying to model in a simple way the contribution due to swell and the contribution due to drawdown and attempting to incorporate elasticity and relaxation effects. With the former, it is possible to make some rigorous predictions, but it is still far from

obtaining a rigorous treatment of the parison formation step. It is possible to make more predictions with the second approach, but the treatment has a number of very restrictive assumptions.

Now regarding the point about the assumption of fully developed flow in the annular die, we have published in the *Journal of Rheology* an analysis of the start-up flow of a viscoelastic material in an annular die, including various geometries. The published treatment yields analytical solutions of the corresponding blow-molding problem, involving unsteady developing flow.

Finally, I agree with you that acceleration effects are important. However, the problem is that the incorporation of acceleration makes the equations nonlinear and therefore difficult to solve. However, for treating real blow-molding problems, it might be necessary to include acceleration in the analysis.

L. A. Utracki. Your experimental data showed good agreement with theory for the initial period, but the agreement became poorer after 60 to 70 seconds. In the theoretical derivation, you did not take into account either surface tension, which may have a small effect, or nonisothermal effects, which should be significant. In other words, 60 seconds after extrusion, obviously the parison temperature is significantly lower, the viscosity

is higher, and the elongation of the parison is becoming progressively smaller than predicted by your isothermal model.

M. E. Ryan. We have incorporated surface tension and a variety of other effects in a detailed treatment of the Newtonian swell problem. Our conclusion based on numerical calculations, was that surface tension plays a relatively minor role. However, we have not incorporated surface tension effects in the simplified treatment of the non-Newtonian melt problem.

Your point regarding nonisothermal effects is certainly valid. It might explain the disagreement observed between experimental and calculated results at long times.

M. R. Kamal. Do you have an explanation for your observation that increasing elasticity leads to an increase in the inflation rate? Also, you have shown distributions of thickness around the perimeter of the molded articles. It is known that variations occur also in the axial direction. Have you dealt with the axial variations in your analysis?

M. E. Ryan. With regard to the effect of elasticity on the inflation rate, I do not have an explanation for that. In terms of the axial variations of thickness, we have made experimental measurements, but we did not incorporate the axial variation into our calculations.

Numerical Simulation of a Single-Screw Plasticating Extruder

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A fully-predictive steady-state computer model has been developed for a single-screw plasticating extruder. Included in the model are a model for solids flow in the feed hopper; a variation of the Darnell and Mol model for the solids conveying zone; a variation of Tadmor's melting model for the melting zone; an implicit finite difference solution of the mass, momentum, and energy conservation equations for the melt-conveying zone of the extruder and die; and a predictive correlation for the extrudate swell at the die exit. A temperature- and shear-rate-dependent viscosity equation is used to describe the melt-flow behavior in the model. The parameters in the viscosity equation are obtained by applying regression analysis to Instron capillary rheometer data. Given the material and rheological properties of the polymer, the screw geometry and dimensions, and the extruder operating conditions, the following are predicted: flow rate of the polymer, pressure and temperature profiles along the extruder screw channel and in the die, and extrudate swell at the die exit. The predictions have been confirmed with experimental results from a 1½ in. (38 mm) diameter, 24:1 L/D single-screw extruder with a 3/16 in. (4.76 mm) diameter cylindrical rod die. High- and low-density polyethylene resins were used.

INTRODUCTION

The development of mathematical models for single-screw plasticating extruders has been covered extensively in the literature (1-7). By far, the majority of these studies have concentrated on melt extruders or the melt-conveying section of plasticating extruders. The main reason for this is that the analysis and modeling of melt flow is far simpler than that of solids conveying and melting of the polymer. Applications for melt-fed extruders can be found in the polymer-processing industry; for example, in the homogenization and pelletization of the polymer immediately after polymerization. Most extruders used in the plastics industry, however, are plasticating extruders; that is, they are fed by polymer in solid granular form. The solid polymer granules flow by gravity in the hopper and into the screw channel, where they are compressed, conveyed down the screw channel, and then melted.

Modeling of a plasticating extruder should include the analysis of (5):

- gravitational flow behavior of particulate solids in hoppers (in particular, pressure distribution, arching, and bridging);

- stress and temperature distribution in the solids-conveying zone;
- rate of melting, mean width profile of the solid bed (solid-bed profile), and mean temperature of the melt flow into the melt pool in the melting zone;
- drag-induced pressurization and laminar mixing of the melt in both the melt-conveying zone and the melt pool in the melting zone;
- power consumption in the solids-conveying, melting, and melt-conveying zones;
- pressure flow in the die;
- surging conditions; and
- extrudate swelling at the die exit.

In more general terms, one should be able to obtain velocity, temperature, and stress profiles in both the solid and melt phases, from which all the other variables of interest could then be calculated.

It is our objective in this article, to describe a fully predictive computer model of a single-screw plasticating extruder (developed at the Department of Chemical Engineering, McMaster University) and to present the results of simulations and experimental runs on a 1½ in. (38 mm) diameter, 24:1 L/D single-screw extruder. The model, as compared to other extruder models described in the literature (1-7), is unique in that it is fully predictive and in-

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cludes all the extrusion steps from the feed hopper to the swelling of the extrudate at the die exit. Given the material and rheological properties of the polymer, the screw geometry and dimensions, and the extruder operating conditions (screw speed and barrel-temperature profile), the model is used to predict:

- flow rate of the polymer;
- pressure and temperature profiles along the extruder screw channel and in the die; and
- extrudate swell at the die exit.

DESCRIPTION OF THE EXTRUDER MODEL

The computer model consists of six interdependent sections, as shown in Fig. 1: the feed hopper; the solids-conveying, melting, and melt-conveying zones; the die; and the swelling of the extrudate at the die exit. Each of these sections is described below.

Feed Hopper

Solid polymer pellets are fed into the extruder screw channel through the feed hopper, usually by gravity. The base pressure in the feed hopper may be determined by analyzing the pressure distribution in the solids. Walker (8) has derived relationships for the pressure distribution in both vertical and convergent bins, assuming stress equilibrium in the solid particles. Equations 1 and 2, shown below, are used in combination to calculate the pressure at the base of a hopper with square cross-section, as illustrated in Figure 2.

Vertical Sections:

$$p = p_o \exp\left(-\frac{4BD^*H}{W}\right) + \frac{\rho_{bulk}gW}{4BD^*} \left[1 - \exp\left(-\frac{4BD^*H}{W}\right)\right] \quad (1)$$

where

$$B = \frac{\sin \delta \sin \kappa_o}{1 - \sin \delta \cos \kappa_o}$$

$$\kappa_o = \beta_w + \arcsin\left(\frac{\sin \beta_w}{\sin \delta}\right), \arcsin > \frac{\pi}{2}$$

$$\beta_w = \arctan(f_w)$$

and where p and p_o are the pressures at the base and at height H in the vertical section, W the hopper width, ρ_{bulk} the bulk density of the solid polymer particles, g the gravitational acceleration, D^* the distribution factor

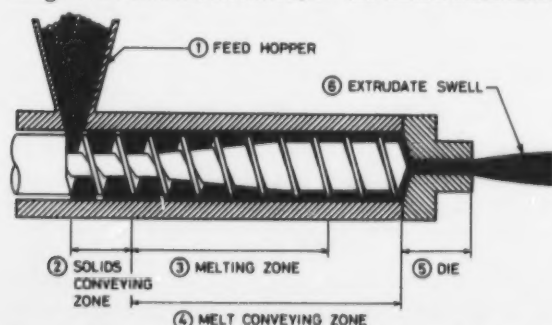


Fig. 1. Schematic diagram of a plasticating extruder showing the components of the present computer model.

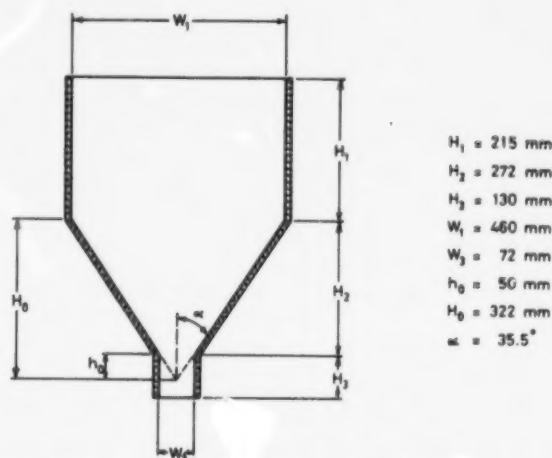


Fig. 2. Geometry and dimensions of a feed hopper with square cross-section.

relating the average vertical stress with the vertical stress near the wall (and assumed to be unity as a first approximation), δ the effective angle of friction of the solid particles, and f_w the static coefficient of friction at the hopper wall.

Convergent Section:

$$p = \left(\frac{h_o}{H_o}\right)^{\psi} p_o + \frac{\rho_{bulk}g h_o}{\psi - 1} \left[1 - \left(\frac{h_o}{H_o}\right)^{\psi-1}\right] \quad (2)$$

where

$$\psi = \frac{2B'D^*}{\tan \alpha}$$

$$B' = \frac{\sin \delta \sin (2\alpha + \kappa_o)}{1 - \sin \delta \cos (2\alpha + \kappa_o)}$$

$$\kappa_o = \beta_w + \arcsin\left(\frac{\sin \beta_w}{\sin \delta}\right), \arcsin < \frac{\pi}{2}$$

$$\beta_w = \arctan(f_w)$$

and where p and p_o are the pressures at the base and top of the convergent section, h_o and H_o are the heights in the convergent section (as shown in Fig. 2), and 2α is the hopper angle.

Solids Conveying Zone

The solids-conveying mechanism in screw extruders is one of drag-induced flow; that is, flow due to the frictional drag of the barrel and screw surfaces on the solid polymer granules. Darnell and Mol (9) were the first to obtain solutions for the solids-conveying zone in screw extruders. More recently, there have been various refinements applied to their one-dimensional plug flow model by Schneider (10), Tadmor and Broyer (11, 12), and Lovegrove and Williams (13-15).

In the solids-conveying model described here, we assume that the solid bed is isothermal and travels as a solid plug with constant velocity. The stress distribution is assumed to be isotropic; that is, the pressure varies only in the downstream direction. By applying a force and torque balance on a differential element of the solid bed in the down-channel direction, the pres-

sure in the solids conveying zone is expressed in the form:

$$p = p_0 e^{-\lambda z} \quad (3)$$

where

$$\lambda = \frac{A_1 K - B_1}{A_2 K + B_2}$$

$$A_1 = f_b W_b \sin \phi + 2Hf_s \sin \theta_b + W_s f_s \sin \theta_s$$

$$A_2 = H W_a \sin \theta_a$$

$$B_1 = f_b W_b \cos \phi - 2Hf_s \frac{D_a}{D_b} \sin \theta_b \cotan \theta_a - W_s f_s \frac{D_s}{D_b} \sin \theta_s \cotan \theta_a$$

$$B_2 = H W_a \frac{D_a}{D_b} \cos \theta_a$$

$$K = \frac{D_a}{D_b} \frac{\sin \theta_a + f_s \cos \theta_a}{\cos \theta_a - f_s \sin \theta_a}$$

and where p_0 is the base pressure in the feed hopper, z_b is down-channel distance at the barrel surface in the solids-conveying zone (as shown in Fig. 3), f_b and f_s are the dynamic coefficients of friction between the solid polymer particles and the barrel and screw surfaces, H is the screw channel depth, W_b and W_s are the channel widths at the barrel surface and screw root, θ_b and θ_s are the helix angles at the barrel surface and screw root, D_b is the inside diameter of the barrel, D_s is the outside diameter of the screw at the root, and W_a , D_a , and θ_a are (respectively) the average channel width, diameter, and helix angle measured at the midpoint between the barrel and screw-root surfaces. The angle ϕ , formed between the tangential velocity of the barrel surface and the down-channel velocity of the solid particles, is given by:

$$\tan \phi = \frac{\pi^2 N \tan \theta_b}{G \rho_{bulk} H D_b (D_b - H) \tan \theta_b \left(\frac{W_a}{W_a + e} \right) - 1} \quad (4)$$

where N is the frequency of screw rotation, G is the mass flow rate of the polymer solids, and e is the screw flight width.

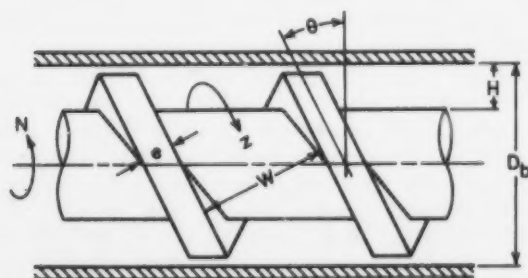


Fig. 3. Geometry of an extruder screw showing characteristic dimensions.

Melting Zone

The melting mechanism in screw extruders was first formulated by Tadmor (4, 5, 16) on the basis of visual observations. More sophisticated models have since been reported by Edmondson and Fenner (17), Shapiro, *et al.* (18, 19), the Lindt (20, 21). In the melting zone, the solid and melt phases coexist. The two phases are clearly segregated from each other, with the melt phase accumulating in a melt pool at the rear flight and the solids segregated as a solid bed at the front flight as, illustrated in Fig. 4. In addition, there exists a thin film of melt between the barrel surface and the solid bed. Due to the proximity of the heated barrel and the intense shear, much of the melting occurs in this melt film. The motion of the barrel relative to the solid bed drags the melt in this film into the melt pool. The width of the melt pool gradually increases in the down-channel direction.

Tadmor's melting model has been used as a basis for the model described in this paper. The delay in melting (that is, the down-channel distance between the start of barrel heating and the appearance of the melt pool) is obtained from an empirical correlation based on experimental data (4). It is assumed that the downstream bed velocity is constant and that the thickness of the upper melt film is independent of cross-channel position. A temperature- and shear-rate-dependent viscosity relation is used to calculate the temperature profile in the melt film. Mass and energy balances on the melt film and solid bed are carried out to obtain the following equations for the rate of melting and the solid-bed profile (22):

Rate of melting:

$$\omega = \Phi \left(\frac{dT}{dy} \right)_{y=0} X \quad (5a)$$

$$= \left| \frac{V_{bx}}{2} \right| \rho_m \delta \quad (5b)$$

where

$$\Phi = \frac{k_m}{C p_s (T_{melt} - T_{sol}) + \lambda + C p_m (T_{bulk} - T_{melt})}$$

$\left(\frac{dT}{dy} \right)_{y=0}$ = temperature gradient in the melt film at the solid-melt interface (and a function of the melt film thickness δ)

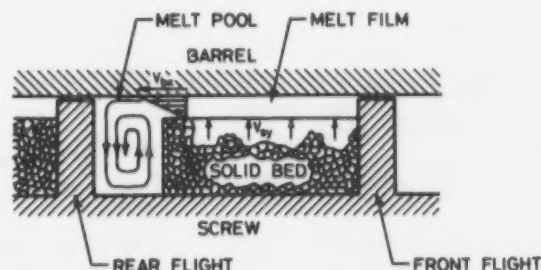


Fig. 4. Idealized cross-section of screw channel in the melting zone. V_{bx} is the component of barrel velocity in the cross channel direction, and V_{sy} is the velocity of the solid bed moving into the solid-melt interface.

and where X is the width of the solid bed, V_{bx} is the cross-channel component of the barrel velocity, T_{bulk} is the flow-average (bulk) temperature of the melt film, T_{melt} is the melting temperature of the polymer, T_{sol} is the temperature of the solid bed far away from the interface, ρ_m is the melt density, Cp_m and Cp_s are the specific heats of the polymer melt and solid, respectively, k_m is the thermal conductivity of the melt, and λ is the heat of fusion of the polymer.

Solid bed profile:

$$\frac{d(H^*X)}{dz} = \frac{-\omega}{\rho_s V_{sz}} = \frac{-\Phi}{\rho_s V_{sz}} \left(\frac{dT}{dy} \right)_{y=0} X \quad (6)$$

where $H^* = H - \delta$, ρ_s is the solid polymer density, and V_{sz} is the down-channel velocity of the solid bed. Equations 5b and 6 are solved simultaneously using a fourth-order Runge-Kutta method to obtain the solid-bed profile X/W as a function of the down-channel direction in the screw channel.

Melt Conveying Zone

Two distinct melt-conveying regions may be found in plasticating extruders. One is downstream of the melting zone after completion of melting and occupies the entire width of the screw channel. The other occurs in the melt pool, extending side by side with the solid bed in the melting zone. Here, the width of the melt pool changes in the down-channel direction. The mass flow rate of the melt also changes as a result of the influx from the melt film.

Due to the helical geometry of the extruder screw and the relative motions of the barrel and screw, the flow pattern of the polymer melt in the screw channel is quite complex and may be described as a "helix within a helix." In order to solve this complex flow problem, several simplifying assumptions are made. It is convenient to pick a coordinate system relative to the screw. Also, one may treat the barrel as rotating about a stationary screw, a valid procedure because gravity and centrifugal inertia forces are negligible in comparison with viscous and pressure forces in the screw channel. Another standard assumption is to consider the helical screw channel as "unwound" and rectilinear. This is a valid assumption because, in most single-screw extruders, the screw channel is relatively shallow in the melt-flow regions. In the analysis of melt flow, it is also standard procedure to introduce the lubrication approximation (23). This involves the local replacement of the actual flow in the parallel or nearly parallel gap between smooth surfaces by uniform flow between plane parallel surfaces.

As stated earlier in this article, by far the majority of studies on extrusion theory in the literature have dealt with the analysis of melt flow. Griffith (24), Zamodits and Pearson (25), and Fenner (6) obtained numerical solutions for fully developed, two-dimensional, nonisothermal, and non-Newtonian flow of melts in infinitely wide rectangular screw channels. For a similar type of flow, Martin (26) presented a solution that allows for the finite width of the channel. Yates (27) and Fenner (28) have developed two-dimensional,

nonisothermal, and non-Newtonian solutions for infinitely wide rectangular screw channels in which the temperature profiles are developing along the channel. For a more complete discussion of extruder models, one is referred to a review by Fenner (7) that, in addition to melt flow in extruders, also covers the analysis of solids conveying and melting.

In the melt-conveying model described here, the following equations of conservation of mass, momentum, and energy in simplified form, together with the accompanying boundary conditions, are solved simultaneously.

Mass (integrated form):

$$\int_0^H v_x dy = 0 \quad (7)$$

$$\int_0^H v_z dy = \frac{Q}{W} \quad (8)$$

Momentum:

$$-\frac{\partial p}{\partial x} + \frac{\partial \tau_{yx}}{\partial y} = 0 \quad (9)$$

$$-\frac{\partial p}{\partial z} + \frac{\partial \tau_{yz}}{\partial y} = 0 \quad (10)$$

Energy:

$$\rho_m Cp_m v_z \frac{\partial T}{\partial z} = k_m \frac{\partial^2 T}{\partial y^2} + \tau_{yx} \frac{\partial v_x}{\partial y} + \tau_{yz} \frac{\partial v_z}{\partial y} \quad (11)$$

Boundary conditions:

$$\begin{aligned} z = 0 \quad p = p_0 \quad T = T_0 \\ y = 0 \quad v_x = v_z = 0 \quad T = T_b \\ y = H \quad v_x = V_{bx} \quad v_z = V_{bz} \quad T = T_b \end{aligned} \quad (12)$$

where Q/W is the flow rate of the melt per unit width of the flow channel, p_0 and T_0 are the pressure and temperature, respectively, at the beginning of the melt flow region, T_b is the barrel temperature (which may also be specified as a function of the down-channel direction), and V_{bx} and V_{bz} are the cross- and down-channel components of the barrel velocity. The following temperature- and shear-rate-dependent constitutive relation is used:

$$\tau_{yx} = \eta \frac{\partial v_x}{\partial y} \quad (13)$$

$$\tau_{yz} = \eta \frac{\partial v_z}{\partial y} \quad (14)$$

$$\log \eta = a_0 + a_1 \log \dot{\gamma} + a_2 (\log \dot{\gamma})^2 + a_3 T + a_4 T^2 + a_5 T \log \dot{\gamma} \quad (15)$$

where

$$\dot{\gamma} = \sqrt{\left(\frac{\partial v_x}{\partial y} \right)^2 + \left(\frac{\partial v_z}{\partial y} \right)^2}$$

The viscosity relation is obtained by curve-fitting Instron capillary rheometer data, as shown in Figs. 5 and 6, to Eq 15 using linear regression. It should be noted that, by retaining the convective term in the en-

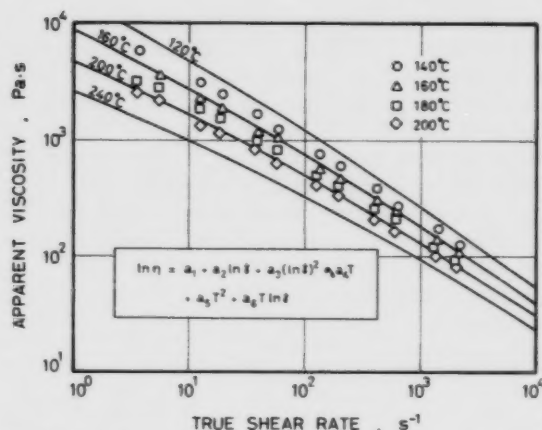


Fig. 5. Viscosity curves for LDPE. Data points represent viscosities measured with an Instron capillary rheometer. Solid curves denote the general viscosity equation (see inset)—parameters a_1 to a_6 are obtained by linear regression.

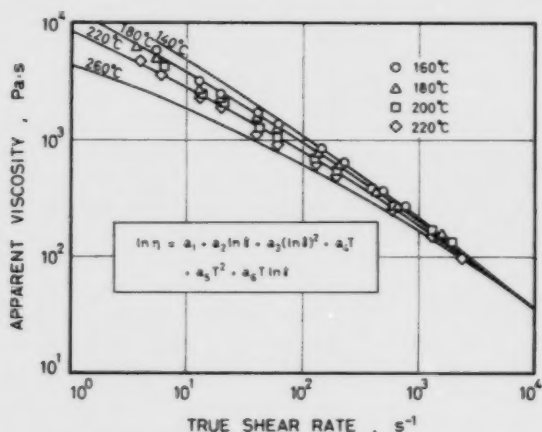


Fig. 6. Viscosity curves for HDPE. Data points represent viscosities measured with an Instron capillary rheometer. Solid curves denote the general viscosity equation (see inset)—parameters a_1 to a_6 are obtained by linear regression.

ergy equation, developing temperature profiles along the screw channel are calculated.

The conservation equations shown above are solved by an implicit finite-difference technique to obtain cross- and down-channel velocity profiles, temperature profiles, and the down-channel pressure profile (22). In addition to viscosity, the polymer properties required for the model are thermal conductivity, density, and specific heat of the melt.

Breaker Plate, Adapter, and Die

The adapter and die used in this study are illustrated in Figs. 7 and 8. The adapter contains a $3/4$ in. $\times$ $3/8$ in. (19.1 mm $\times$ 9.5 mm) rectangular slit channel, whereas the die has a $3/16$ in. (4.76 mm) diameter channel of circular cross-section. For the breaker plate, adapter, and die, the melt-flow analysis is essentially the same as described for the melt-conveying section of the extruder, with the exception that only the down-channel components of velocity are considered and that there are no moving boundaries. The following conservation

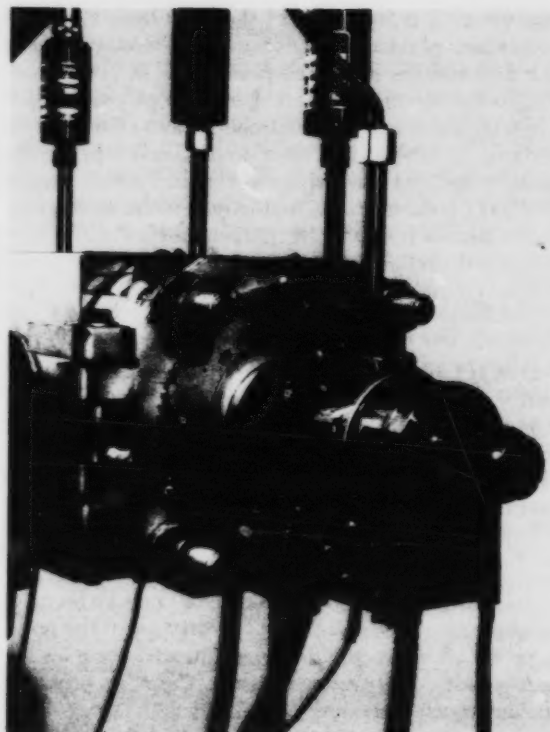


Fig. 7. Photograph of adapter and die.

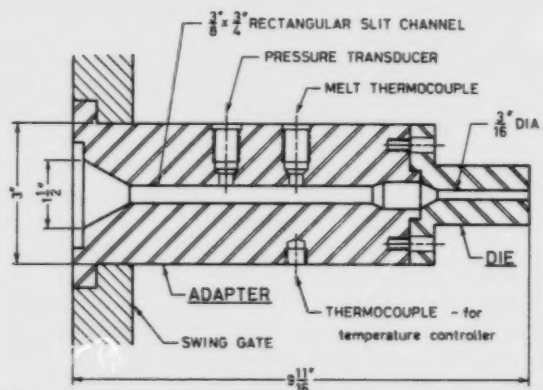


Fig. 8. Schematic diagram of adapter and die.

equations, in simplified form, for the breaker plate, adapter, and die are solved simultaneously:

Breaker Plate

Mass (integrated form):

$$\int_0^{n_{Br}} v_z r dr = \frac{Q}{2\pi N_{Br}} \quad (16)$$

Momentum:

$$-\frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) = 0 \quad (17)$$

Energy:

$$\rho_m C_{pm} v_z \frac{\partial T}{\partial z} = \frac{k_m}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \tau_{rz} \frac{\partial v_z}{\partial r} \quad (18)$$

Boundary conditions:

$$\begin{aligned} z = 0 \quad p = p_o \quad T = T_o \\ r = 0 \quad \frac{\partial v_z}{\partial r} = 0 \quad \frac{\partial T}{\partial r} = 0 \\ r = R_{Br} \quad v_z = 0 \quad \frac{\partial T}{\partial r} = 0 \end{aligned} \quad (19)$$

where N_{Br} is the number of holes in the breaker plate, R_{Br} is the radius of each hole, and p_o and T_o are the pressure and bulk temperature of the polymer melt at the end of the extruder screw channel.

Adapter

Mass (integrated form):

$$\int_0^{H_A/2} v_z dy = \frac{Q}{2W_A} \quad (20)$$

Momentum:

$$-\frac{\partial p}{\partial z} + \frac{\partial \tau_{yz}}{\partial y} = 0 \quad (21)$$

Energy:

$$\rho_m C p_m v_z \frac{\partial T}{\partial z} = k_m \frac{\partial^2 T}{\partial y^2} + \tau_{yz} \frac{\partial v_z}{\partial y} \quad (22)$$

Boundary conditions:

$$\begin{aligned} z = 0 \quad p = p_o \quad T = T_o \\ y = 0 \quad \frac{\partial v_z}{\partial y} = 0 \quad \frac{\partial T}{\partial y} = 0 \\ y = \frac{H_A}{2} \quad v_z = 0 \quad T = T_A \end{aligned} \quad (23)$$

where H_A and W_A are (respectively) the height and width of the rectangular flow channel, p_o and T_o are the pressure and bulk temperature of the melt at the end of the breaker plate, and T_A is the temperature of the adapter.

Die

Mass (integrated form):

$$\int_0^{R_D} v_z r dr = \frac{Q}{2\pi} \quad (24)$$

Momentum:

$$-\frac{\partial p}{\partial z} + \frac{1}{r} \frac{\partial}{\partial r} (r \tau_{rz}) = 0 \quad (25)$$

Energy:

$$\rho_m C p_m v_z \frac{\partial T}{\partial z} = \frac{k_m}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) + \tau_{rz} \frac{\partial v_z}{\partial r} \quad (26)$$

Boundary conditions:

$$\begin{aligned} r = 0 \quad \frac{\partial v_z}{\partial r} = 0 \quad \frac{\partial T}{\partial r} = 0 \\ r = R_D \quad v_z = 0 \quad T = T_D \end{aligned} \quad (27)$$

where R_D is the radius of the circular flow channel in the die, and T_D is the die temperature.

An implicit finite-difference method is used to solve the conservation equations shown above to obtain veloc-

ity, temperature, and pressure profiles in the breaker plate, adapter, and die (22). As in the extruder screw channel, the polymer properties required for the calculations are viscosity, thermal conductivity, density, and specific heat of the melt.

Extrudate Swell

Polymer melts, due to their viscoelastic behavior, exhibit an increase in cross-sectional area whenever they emerge from a die, provided that there is no subsequent drawing. This phenomenon is usually called extrudate swell. Depending on the extrusion conditions, the die geometry and dimensions, and the rheological properties of the polymer, the increase in extrudate diameter (in the case of a circular die) may range from 1.5 to 4 times the die diameter.

There seems to be a general agreement that extrudate swell is mainly due to a sudden recovery of stored elastic energy and a subsequent stress relaxation. However, no single theory of extrudate swell seems to be generally accepted. A review paper by Vlachopoulos (29) has recently been published on extrudate swell of polymers. It is concluded that, despite the large number of investigations on extrudate swell, the existing models do not provide a clear picture as to the importance of the various rheological parameters. There is still disagreement regarding the molecular structure effects for many polymers. The interrelations between molecular, rheological, and geometrical parameters and their effect on extrudate swell are not well-understood. A fully predictive theory has yet to be developed.

In the model described here, the prediction of extrudate swell for the circular die is based on Tanner's elastic recovery theory (30), studies by White, *et al.* (31-33), and by Racine and Bogue (34), and measurements of extrudate swell performed on an Instron capillary rheometer. Tanner's equation for extrudate swell may be expressed as:

$$\frac{d}{D} = \left[\frac{\int_0^R (N_1 + G - \frac{\tau^2}{G}) r dr}{\int_0^R G r dr} \right]^{1/8} + 0.12 \quad (28)$$

where N_1 is the first normal stress difference, G is an elastic modulus, and τ is the shear stress. Equation 28 may be written as:

$$\frac{d}{D} = \left[\frac{\int_0^{r_w} [N_1(\tau) + G(\tau) - \frac{\tau^2}{G(\tau)}] \tau d\tau}{\int_0^{r_w} G(\tau) \tau d\tau} \right]^{1/8} + 0.12 \quad (29)$$

Assuming that:

$$N_1 = A\tau^b \quad (30)$$

$$G = \frac{2\tau^2}{N_1} \quad (31)$$

and substituting Eqs 30 and 31 into Eq 29, one obtains the following equation for the prediction of extrudate swell for an extruder die with circular cross-section:

$$\frac{d}{D} = \left[\frac{A^2}{4} \frac{(4-b)}{(2+b)} \tau_w^{2b-2} + 1 \right]^{1/6} + 0.12 \quad (32)$$

The parameters A and b are obtained by curve-fitting Eq 32 to the Instron capillary extrudate swell data using nonlinear regression, as shown in Figs. 9 and 10.

RESULTS OF SIMULATIONS AND EXPERIMENTS

The present computer model was used to simulate a 1½ in. (38 mm) diameter, 24:1 L/D single-screw plasticating extruder. Various screw speeds and barrel-temperature profiles were used for both high- and low-density polyethylene resin. The simulations were confirmed with experimental runs on a Killion single-screw extruder. For each run, pressure measurements at three locations (two in the screw channel and one in the adapter) were obtained using Dynisco transducers, and the melt temperature was measured in the adapter using a melt thermocouple. The mass-flow rate of the polymer and the extrudate swell at the die exit were also measured.

Results of the computer simulations and experimental measurements are presented in Tables 1 to 4 and

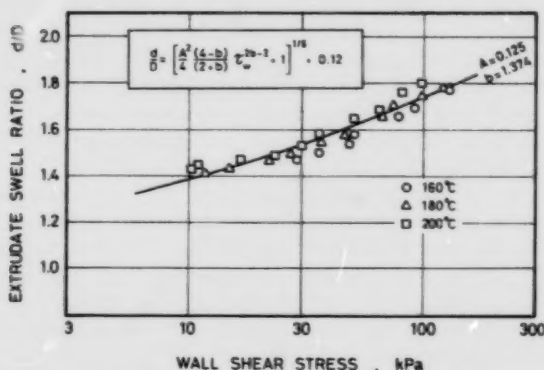


Fig. 9. Extrudate swell correlation for LDPE. Data points represent extrudate swells measured on an Instron capillary rheometer. Solid curve denotes the extrudate swell equation (see inset)—parameters A and b are obtained by nonlinear regression.

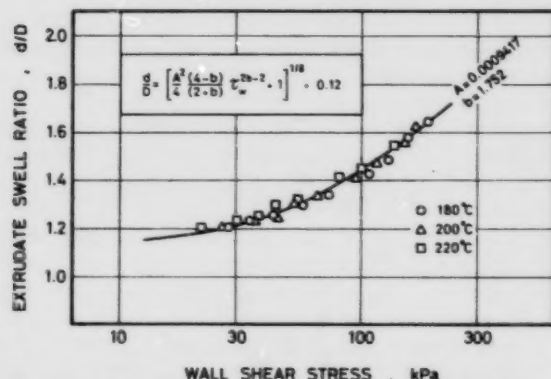


Fig. 10. Extrudate swell correlation for HDPE. Data points represent extrudate swells measured on an Instron capillary rheometer. Solid curve denotes the extrudate swell equation (see inset)—parameters A and b are obtained by nonlinear regression.

Table 1. Predicted vs. Measured Mass-Flow Rates for LDPE

Screw speed, rpm	Mass-flow rate, kg/s	
	Predicted	Measured
40	$1.965 \cdot 10^{-3}$	$1.911 \cdot 10^{-3}$
60	$2.929 \cdot 10^{-3}$	$2.948 \cdot 10^{-3}$
80	$3.886 \cdot 10^{-3}$	$3.968 \cdot 10^{-3}$

Table 2. Predicted vs. Measured Mass-Flow Rates for HDPE

Screw speed, rpm	Mass-flow rate, kg/s	
	Predicted	Measured
40	$1.881 \cdot 10^{-3}$	$1.755 \cdot 10^{-3}$
60	$2.812 \cdot 10^{-3}$	$2.707 \cdot 10^{-3}$
80	$3.748 \cdot 10^{-3}$	$3.705 \cdot 10^{-3}$

Table 3. Predicted vs. Measured Extrudate Swell for LDPE

Screw speed, rpm	Extrudate swell, d/D	
	Predicted	Measured
40	1.692	1.646
60	1.721	1.674
80	1.742	1.713

Table 4. Predicted vs. Measured Extrudate Swell for HDPE

Screw speed, rpm	Extrudate swell, d/D	
	Predicted	Measured
40	1.692	1.646
60	1.721	1.674
80	1.742	1.713

Figs. 11 to 16 for two polymers: low-density polyethylene (Union Carbide Canada Ltd., DFDY 4400) and high-density polyethylene (DuPont Canada Inc., SCLAIR 19A). The extruder screw dimensions, processing conditions, and polymer properties are listed in Tables 5 to 7. The feed hopper and die dimensions are given in Figs. 2 and 8, respectively.

In Tables 1 and 2, the predicted and measured mass-flow rates for LDPE and HDPE are compared at three

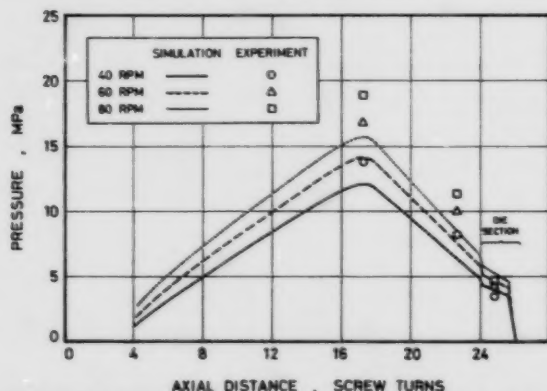


Fig. 11. Predicted down-channel pressure profiles in the extruder screw channel and die section for LDPE. Data points represent melt-pressure measurements in the extruder and adapter.

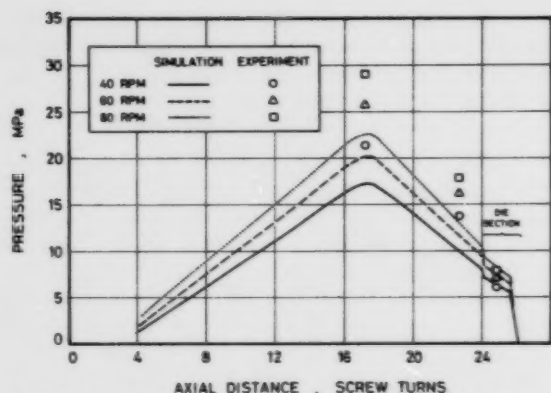


Fig. 12. Predicted down-channel pressure profiles in the extruder screw channel and die section for HDPE. Data points represent melt-pressure measurements in the extruder and adapter.

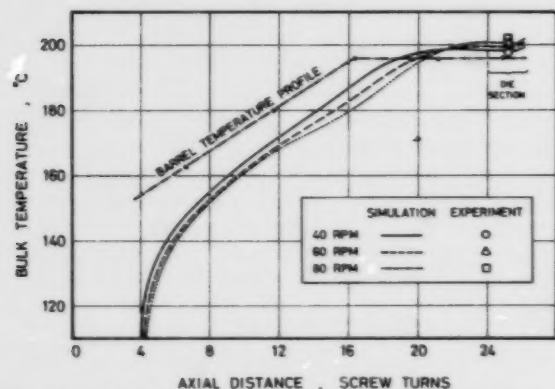


Fig. 13. Predicted down-channel bulk temperature profiles in the extruder screw channel and die section for LDPE. Data points represent melt temperature measurements in the adapter.

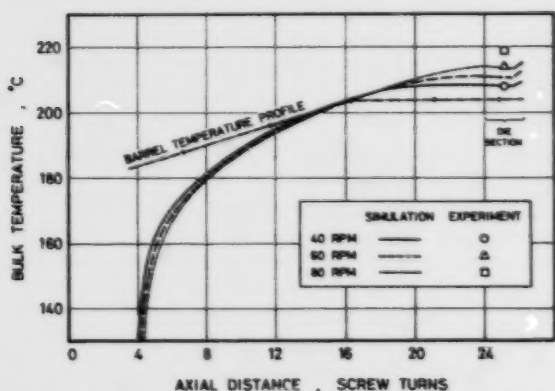


Fig. 14. Predicted down-channel bulk temperature profiles in the extruder screw channel and die section for HDPE. Data points represent melt temperature measurements in the adapter.

Frequencies of screw rotation: 40, 60, and 80 rpm. In the case of the LDPE, the predicted and measured values differ by 1 to 3 percent; for the HDPE, the difference ranges between 1 and 7 percent. Down-channel pressure profiles for the two resins are presented in Figs. 11 and 12, and are compared with the melt pressure mea-

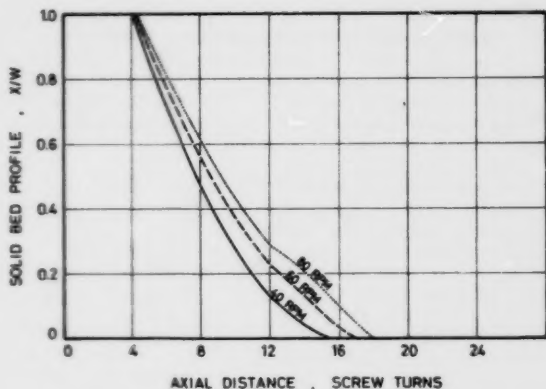


Fig. 15. Predicted solid-bed profiles in the extruder screw channel for LDPE.

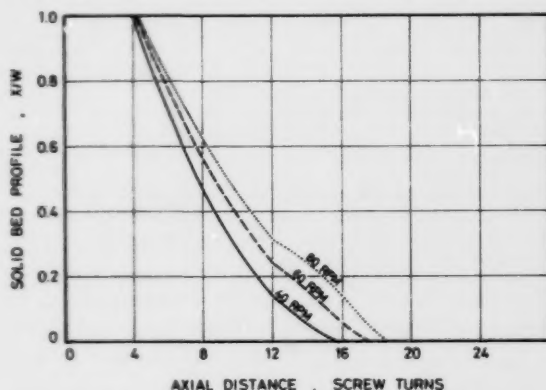


Fig. 16. Predicted solid-bed profiles in the extruder screw channel for HDPE.

surements in the extruder and adapter. As compared to the measured pressure values, the predicted profiles are lower in the screw channel and higher in the adapter. The differences range between 12 and 25 percent for the LDPE, and between 7 and 27 percent for the HDPE. In Figs. 13 and 14, the down channel bulk temperature profiles for the two resins are presented, along with the melt temperature measurements in the adapter. The difference between the predicted and measured temperature values range between 1° and 2°C for the LDPE, and between 1° and 5°C for the HDPE. No measurements of melt temperature were made in the extruder screw channel. Predicted solid-bed profiles are shown in Figs. 15 and 16 for the two resins. However, experimental verification of these predictions was not performed. Finally, the predicted and measured values of extrudate swell at the die exit are compared in Tables 3 and 4. The difference between the predicted and measured values is approxi-

Table 5. Extruder Screw Geometry and Dimensions

Square-pitch screw	
Feed/compression/metering sections	12/6/6 turns
Barrel inside diameter, D_b	1.50 in. (38.1 mm)
Screw lead	1.50 in. (38.1 mm)
Channel depth in feed section	0.24 in. (6.1 mm)
Channel depth in metering section	0.06 in. (2.0 mm)
Flight width	0.25 in. (6.35 mm)

Numerical Simulation of a Single-Screw Plasticating Extruder

Table 6. Material Properties and Processing Variables for LDPE (Union Carbide Canada Ltd., DFDY 4400)

Extruder operating conditions	
Barrel temperature profile	163/179/196/196/196°C
Frequency of screw rotation	40, 60, and 80 rpm
Material and rheological properties	
Static coefficient of friction, f_w	0.30
Effective angle of friction, δ	33.7°
Dynamic coefficient of friction, f_b	0.40
Dynamic coefficient of friction, f_s	0.25
Heat capacity—melt, C_{p_m}	2595 J/(kg · K)
—solid, C_{p_s}	2763 J/(kg · K)
Density—bulk, ρ_{bulk}	595 kg/m ³
—melt, ρ_m	779 kg/m ³
—solid, ρ_s	919 kg/m ³
Thermal conductivity—melt, k_m	0.182 W/(m · K)
Heat of fusion, λ	129785 J/kg
Melting temperature, T_{melt}	110°C
Viscosity, η (see Fig. 5)	a_1 11.7838
	a_2 -0.639104
	a_3 -0.0112744
	a_4 -0.0183449
	a_5 8.78448 · 10 ⁻⁶
	a_6 9.66512 · 10 ⁻⁴
where η [Pa · s], $\dot{\gamma}$ [s ⁻¹], T [°C]	
Extrudate swell correlation A (see Fig. 9)	0.125
	b 1.374

Table 7. Material Properties and Processing Variables for HDPE (DuPont Canada Inc., SCLAIR 19A)

Extruder operating conditions	
Barrel temperature profile	188/196/204/204/204°C
Frequency of screw rotation	40, 60, and 80 rpm
Material and rheological properties	
Static coefficient of friction, f_w	0.30
Effective angle of friction, δ	33.7°
Dynamic coefficient of friction, f_b	0.40
Dynamic coefficient of friction, f_s	0.25
Heat capacity—melt, C_{p_m}	2512 J/(kg · K)
—solid, C_{p_s}	2303 J/(kg · K)
Density—bulk, ρ_{bulk}	595 kg/m ³
—melt, ρ_m	777 kg/m ³
—solid, ρ_s	960 kg/m ³
Thermal conductivity—melt, k_m	0.182 W/(m · K)
Heat of fusion, λ	201189 J/kg
Melting temperature, T_{melt}	130°C
Viscosity, η (see Fig. 6)	a_1 9.95345
	a_2 -0.782449
	a_3 -0.0114677
	a_4 4.50087 · 10 ⁻³
	a_5 -3.93029 · 10 ⁻⁵
	a_6 1.41590 · 10 ⁻³
where η [Pa · s], $\dot{\gamma}$ [s ⁻¹], T [°C]	
Extrudate swell correlation A (see Fig. 10)	9.417 · 10 ⁻⁴
	b 1.752

mately 2 percent for the LDPE and 10 percent for the HDPE.

Further refinements of the extruder model, especially in the solids-conveying zone and in the initial stages of the melt-conveying zone, should minimize the differences between the predicted and measured values given above. A parameter sensitivity study was also performed for each of the polymer properties utilized in the overall model. The polymer property data were individually changed by 2 percent, and their effect on the overall extruder performance was examined in each case. It was seen that changes in the dynamic coefficients of friction and melt density had the greatest effect, especially on mass-flow rate and pres-

sure development in the extruder screw channel. More accurate values of these properties would also improve the overall extruder model results.

CONCLUDING REMARKS

A fully-predictive computer model for a single-screw plasticating extruder has been developed to predict the flow rate of the polymer, pressure, and temperature profiles along the extruder flow channel in the die and in the extrudate swell at the die exit. The simulations depend entirely on the material and rheological properties of the polymer, the screw geometry and dimensions, and the operating conditions of the extruder (screw speed and barrel-temperature profile). The simulations are not modified on the basis of temperature or pressure measurements in the extruder. Any size of extruder or screw design within reasonable limits may be simulated by the present computer model.

Finally, it is possible to further improve the overall computer model by improving the individual submodels, especially for the solids-conveying, delay in melting, and the melting sections. However, to improve these submodels, we need more direct experimental evidence on exactly what happens in these subsections. Presently, we cannot justify introducing more sophisticated models until such information becomes available. Also, the additional computation time that may be necessary for the model will be a factor to be considered when introducing such improvements.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada for financial assistance, and DuPont Canada Inc. and Union Carbide of Canada, Limited for their donations of the polyethylene resins used in the experimental runs.

NOMENCLATURE

C_p	= specific heat
d/D	= extrudate swell ratio
D_b, D_s	= screw diameter at barrel surface and at screw root
e	= screw flight width (perpendicular to the flight)
f_b, f_s	= dynamic coefficient of friction at barrel and screw surface
f_w	= static coefficient of friction at feed-hopper wall
g	= gravitational acceleration
G	= mass-flow rate
G	= elastic modulus
H	= screw-channel depth
k	= thermal conductivity
N	= frequency of screw rotation
N_1	= first normal stress difference
p	= pressure
Q	= volumetric flow rate
r	= radial distance in cylindrical coordinates
R	= radius
T	= temperature
T_{bulk}	= bulk (flow-average) temperature

T_{melt}	= melting temperature of polymer
v_x, v_z	= cross-channel and down-channel velocity
V_b	= tangential barrel velocity
W	= screw-channel width (perpendicular to flight)
x	= cross-channel distance
X	= solid-bed width
X/W	= solid-bed profile
y	= distance perpendicular to x - and z -directions
z	= down-channel distance
$\dot{\gamma}$	= shear rate
δ	= effective angle of friction
δ	= thickness of melt film in melting zone
η	= non-Newtonian viscosity
θ	= helix angle
λ	= latent heat of fusion
ρ	= density
$\tau, \tau_{yx}, \tau_{yz}$	= shear stress
ω	= rate of melting per unit down-channel distance

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Discussion of the E. E. Agur Article

W. I. Patterson. This morning we heard Dr. Kamal talk of modeling of injection molding, one of the important achievements that exists for predicting short shots. In modeling extruders, one would want a model that would predict surging. I wonder if your model can do this. Could you comment upon how models could predict extruder surging?

E. E. Agur. Surging cannot be predicted by our model. This is related to the melting model that we have selected. The model assumes a constant velocity of the solid bed in the screw channel. In order to predict surging, one should allow for the acceleration of the solid bed.

Ch. I. Chung. I have two questions. Firstly, in solid conveying, you said that you used the Darnell and Mol equation, in which you need to insert an initial pressure. Depending on the choice of the initial pressure, one can get all sorts of outputs. How did you select this initial pressure? Secondly, in the melting zone, the Tadmor model that you have used assumes a constant solid-plug velocity. For this reason, in order to make pressure computation, you have to make some assumptions again. Here also, depending on what you do, your results will vary. How did you calculate the pressure profile that eventually gave you such a good fit in the output data?

E. E. Agur. First of all, we predicted the pressure at the start of the solids conveying zone by calculating the base pressure at the bottom of the feed-hopper. The whole purpose of adding the feed-hopper to the model was to allow us to calculate the base pressure. As for the pressure profile in the solid-conveying zone, one has to assume a mass-flow rate of the polymer. This assumed value was maintained through the length of the extruder. Using it, we calculated the pressure profile in the solids bed, the pressure profile in the melting and metering zones, and then, finally, the final pressure at the unit of the die. If the computed exit pressure was greater than zero, then we had to assume a new mass flow rate and repeat the calculation until zero exit pressure was obtained.

Ch. I. Chung. In the melting section, you are calculating the pressure profile. However, here you cannot apply the friction model because the polymer is melting. How did you calculate the pressure in this case?

E. E. Agur. We started the melt-conveying zone in parallel with the melting zone. We calculated a pressure profile in the melt pool, and then this was carried in parallel with the melting zone.

V. L. Lenir. Could you give some details as to how you started off this melting zone? I assumed some sort of a delay time. The melt pulled over the top of the solid plug had to reach a certain proportion of the flight clearance.

E. E. Agur. We employed the same method and correlation, as proposed by Tadmor.

V. L. Lenir. You did not take into account the height of the channel. There are two factors that were used by Tadmor, called F_d and F_p , to account for the shape of the flight. Your model assumes an infinite channel width. Is there not any scope for doing some sort of curve fitting for these two factors against the ratio of the channel height to the channel width for non-Newtonian systems?

E. E. Agur. As long as one deals with Newtonian fluids, then it is possible to combine the shape factors for drag and pressure flow in some manner. However, for non-Newtonian systems, it is not possible to obtain simple analytical expressions for the shape factors. Some workers have obtained some numerical correlations between shape factors and aspect ratio for such a situation. In our case, we did not pursue this matter. We discovered that using Newtonian shape factors to deal with a non-Newtonian extrusion situation caused more problems than it solved.

V. L. Lenir. You assumed plug flow in the solids feed zone. One would not expect this to be valid with powder feed. This means that your model applies mainly for pellets.

E. E. Agur. Yes.

L. A. Utracki. From the point of view of rheology, the assumption that only the shear viscosity is to be taken into account is wrong. As I understand it, you are disregarding even the variation of viscosity with pressure. For some polymers, an increase of pressure by 1 kbar changes viscosity by a factor of 1,000. Furthermore, there are experimental data that show that, for two resins having nearly identical shear flow curves, the extruder output varies with normal stress. Nevertheless,

the agreement between theory and the data that you presented is astonishing. The question is: why? Obviously, you have two adjustable parameters for the die swell, but for the extruder output, you do not seem to have any adjustable parameters.

M. R. Kamal. I want to insert one more question. What kind of P-V-T relation did you use, and what kind of variation of properties, besides viscosity, did you allow in your model? Did you consider changes in density and the thermal properties? This must be very important.

E. E. Agur. Such variations are important, but we have assumed constant values for the densities, thermal conductivities, and heat capacities in our model. Good predictions were obtained without the need for adjustable parameters or "fudge factors." The whole point of our model is that it is fully predictive. You are given the screw dimensions and the indicated resin properties, and the model yields a full process prediction.

Ch. I. Chung. The agreement between the measured values and the predictions, as far as extruder output is concerned, look quite good, but the pressure prediction is not. It is interesting to note that both the measured and predicted output values are virtually proportional to screw RPM. It seems that, since a small 1½ in. extruder has been used, substantial melting occurs, and there is not much of a pressure-flow effect. So what you are calculating and measuring is virtually drag flow. The situation may not be so favorable with a larger extruder. I tend to agree with Dr. Utracki that, with these crude assumptions, you are not going to have such a good fit.

E. E. Agur. I agree with you on this point. We have to look at, not only different sizes of extruders, but also different screw designs and different plastics.

On the Dynamics and Control of a Plasticating Extruder

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In recent years, there have been many papers published on the application of process control to plasticating extruders. Much of the literature concentrates on the more classical control techniques. However, recent research has studied the application of stochastic identification techniques for building transfer function models for the extruder. In particular, the relationship of screw speed to die pressure and temperature has been studied. In the present work, both step tests and pseudo-random binary sequence tests were used to study the process dynamics of a 38 mm Killion extruder having a length-to-diameter ratio of 24:1. This study concentrates on the regulation of the extruder pressure in the face of its inherent surging characteristics. Variations in the quality of the feed plastic were studied through pulse and step changes in input polymer composition. Significant control problems resulted from measurement noise, which appeared at the same frequency as the screw rotation speed. Various mathematical filters to reduce the effect of this noise on the control variables were studied.

INTRODUCTION

In recent years, there have been many papers published on the application of process control to plasticating extruders. Many commercial products are extruded, and plastics are constantly finding new applications. With more exacting product specifications and the price of oil-based polymers constantly rising, the need to minimize fluctuations in the operating conditions of the extruder becomes crucial. In addition, for certain polymers, the extruder must be operated under precisely controlled conditions in order to avoid degradation of the plastic.

The literature on dynamics and control of plasticating extruders has been critically reviewed by Costin, *et al.* (1). Hence, only a brief description of the major works is presented here. Much of the literature (2-5) concentrates on the more classical control techniques. However, recently some authors (6-9) have studied the application of stochastic identification techniques to building transfer function models for the extruder.

Parnaby, *et al.* (6, 7), identified two transfer functions: screw speed input to die pressure output and screw speed input to melt temperature output. These models were developed using a pseudo-random binary sequence (PRBS) test in combination with Box and Jenkins (10) times-series analysis techniques. They did not implement the corresponding minimum variance or self-tuning control schemes, although some simulation control studies were done.

Patterson, *et al.* (8-9), attempted similar modeling procedures, one using screw speed (8) as the manipulated variable and the other using a die-constricting valve (9). However, the transfer functions determined were not reported, and control of the extruder was not attempted.

More recently, Hassan and Parnaby (11) implemented a cascade control scheme in which time-series models provided one-step-ahead forecasts of the melt temperature and pressure; quasilinear, steady-state models of the extruder were used to compute the

optimal trajectory to move from one operating point to the next.

In the work presented here, both step tests and PRBS tests were used to model the process dynamics of the extruder. The empirical models of die pressure and melt temperature were related back to the physical phenomena described by Tadmor and Klein (12). The control study presented here concentrated on the regulation of the extruder pressure in the face of its inherent surging characteristics. Standard proportional-integral (PI) controllers were compared to an on-line adaptive controller: the self-tuning regulator. This latter controller adapts to changing process conditions by adjusting the controller parameters in accordance with an on-line, recursive, least-squares algorithm that (theoretically) guarantees optimal performance in a dynamic, as well as a steady-state, sense. Variations in the quality of the feed plastic were also studied by introducing pulse and step changes in input polymer composition. The step changes correspond to the problems encountered in changing from one batch of polymer to another, since different batches frequently have different rheological and chemical characteristics.

EXPERIMENTAL EQUIPMENT

The research was done using a Killion 38 mm extruder having a length-to-diameter (L/D) ratio of 24:1. The extruder has five proportional-integral (PI) temperature controllers, of which four regulate barrel-wall temperatures and the fifth, the die-wall temperature. A thermocouple is positioned in the die so as to measure the melt temperature. Extruder pressure is measured by a strain-gauge-type pressure transducer positioned in the melt-pumping region of the screw, upstream from the breaker plate and adapter. The pressure transducer is connected to a PI controller which, for the purposes of these experiments, was used only as a signal conditioner and amplifier for transmitting pressure measurements to the computer. A schematic of the process equipment is given in Fig. 1. As the extrudate is produced, it drops into a cooling water bath. It is then dried in an air stream and passed through the rollers of a take-up mechanism. The take-up mechanism is also manufactured by Killion, and it uses a SECO 8504 motor-speed controller. Three different types of polymer were used in the various experiments: Union Carbide DNDY-2530, DFDQ-4400, and DFDY-6600 polyethylene. Table 1 lists their specifications.

The extruder was interfaced to one of the Depart-

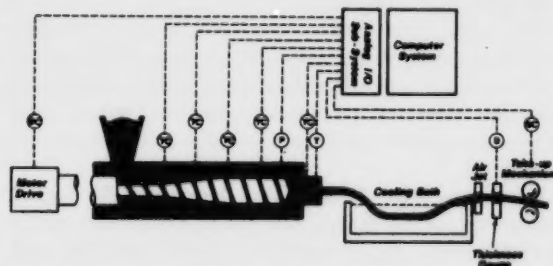


Fig. 1. Schematic diagram of extruder and associated equipment.

Table 1. Polyethylene Polymer Characteristics

Polymer	Melt Index	Specific Gravity
DFDQ4400	20.0	0.9175
DNDY 2530	1.7	0.920
DFDY6600	0.22	0.920

ment of Chemical Engineering minicomputer systems. This consisted of two NOVA 1200 computers, a 10 M-byte moving-head disk, and a ½ M-byte fixed-head disk, with various peripherals such as a CRT, line printer, paper-tape punch and reader, and teletypes.

The measurements recorded by the computer consisted of the five wall temperatures, the melt temperature, the pressure, and the screw speed. The computer was capable of manipulating both the screw speed and the die-heater power.

STEADY-STATE BEHAVIOR

The steady-state pressure behavior of the extruder for polymer DNDY, extruded at approximately 50 r/min, is shown in Fig. 2. These data were recorded in order to determine what type of disturbances are normally associated with the extruder. The disturbances in Fig. 2 consist of oscillations at three different frequencies, which are described in the following paragraphs.

Figure 3 presents the data of Fig. 2 on an expanded time scale. This graph shows that the highest frequency oscillation has a period of approximately 1.2 s. The extruder operating screw speed of 50 r/min correlates with this frequency of noise. Tadmor and Klein (12)

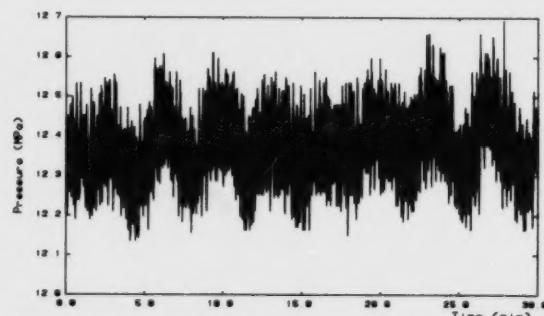


Fig. 2. Extruder steady-state melt pressure behavior.

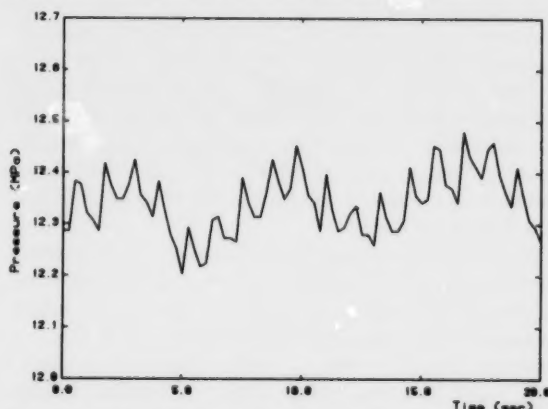


Fig. 3. Extruder steady-state melt pressure behavior: expanded time scale.

have noted that a pressure transducer located near the flight surface would pick up a signal that is caused by the passing of the screw flight but that this noise is not part of the true pressure measurement, as seen in the die. The extruder used for this work was configured with the pressure transducer in this area. Unfortunately, it was impossible to move the pressure transducer to the adapter or to the die so that the effect could be removed, but preliminary results since the work was completed have verified the effect.

Figure 4 shows the data of Fig. 2 after they have been digitally filtered by a fourth-order Butterworth low-pass filter with a cutoff frequency of 0.5 Hz. This filter removes the flight noise from the data, leaving pressure fluctuations with a period of approximately 8 s. These 8 s fluctuations are examples of the intermediate frequency pressure surges discussed by Tadmor and Klein (12). Briefly, these fluctuations are caused by the periodic breaking up of the tip of the solid bed. This process usually occurs at the same point, causing an inherent pressure instability with relatively constant frequency. The period of the surging was found to be unaffected by the extruder screw speed or by the type of polyethylene used. However, the amplitude of the disturbance was observed to depend on the operating region.

Finally, there is a much-longer-term oscillation with a period of approximately 3.0 min, which is visible in Fig. 2. This is due to the cycling of the die temperature controller. Figure 5 shows the melt and the die temperatures for the same experiment as Fig. 2. Although it was suspected that the problem was attributable to excessively tuned parameters on the analog PI controller, the die temperature cycled even with a detuned controller. Schott (13) also reports problems with a cycling temperature controller. Even with the die controller turned off, there was a small amount of cycling in both the melt temperature and pressure.

STEP TESTS

In order to estimate the process-time constant and to determine the system linearity, numerous step tests were performed on the extruder. Although the step tests involved changes in the extruder screw speed, the

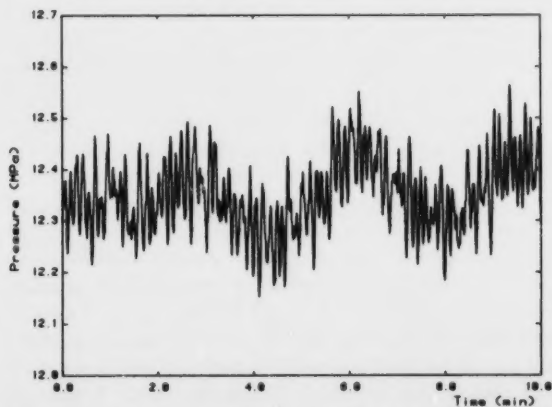


Fig. 4. Extruder steady-state melt pressure behavior: low-pass filtered data.

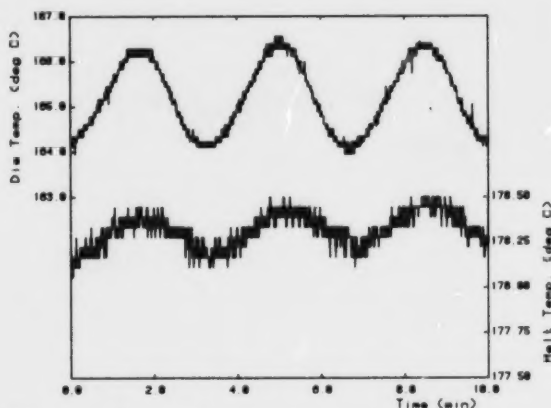


Fig. 5. Steady-state die and melt pressure behavior.

actual manipulated variable was the signal sent from the computer to the extruder motor controller. The computer output signal is reported in scaled units ranging from 0 to 100, corresponding to the extruder operating range of 0 to 100 r/min. This computer output will be referred to as motor power (M.P.).

Figure 6 shows a step change of 8.0 motor power units (52 to 60 M.P.) for DNDY polymer. The screw speed change was approximately 9.0 r/min (49 to 58 r/min). There is a rapid pressure response, but no significant decay in pressure is seen as the temperature settles. The pressure response appears to be completed in one sampling interval. The time constants can be estimated as 0.2 s for pressure and 20 s for temperature, with gains, estimated by averaging the steady-state values of 110 kPa/M.P. and 0.28°C/M.P., respectively. The transfer functions are presented by Eqs 1 and 2:

$$P(s) = \frac{110}{0.2s + 1} U(s) \quad (1)$$

$$T(s) = \frac{0.28}{20s + 1} U(s) \quad (2)$$

Figure 7 shows a similar step of 74 to 80 in motor power. Here, the gains are reduced to 76 kPa/M.P. and 0.19°C/M.P. for pressure and temperature, respectively. The screw speed changed approximately 6.5

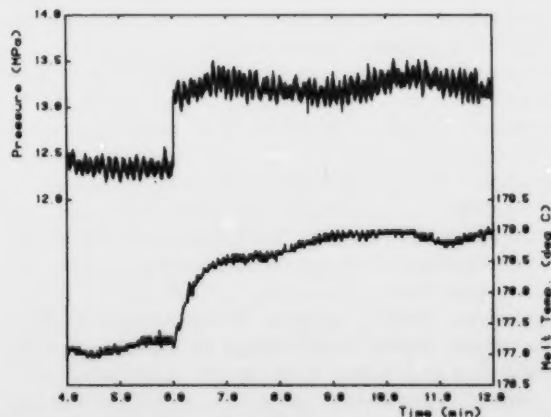


Fig. 6. Step responses of melt pressure and temperature to midrange motor power changes.

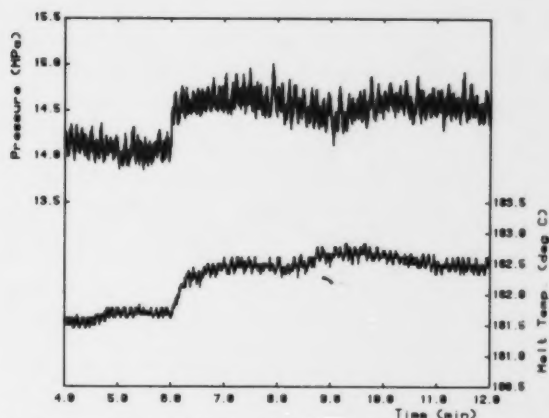


Fig. 7. Step responses of melt pressure and temperature to high-range motor power changes.

r/min. The transfer functions for this case are presented in Eqs 3 and 4:

$$P(s) = \frac{76}{0.25s + 1} U(s) \quad (3)$$

$$T(s) = \frac{0.19}{15s + 1} U(s) \quad (4)$$

Observing the response of the temperature to screw speed steps in Figs. 6 and 7 shows that the mean temperature has moved to a new level. The die temperature controller is unable to maintain the melt temperature at a mean level in the face of screw speed disturbances. This phenomenon will be discussed further when the effect of closed-loop control on the melt temperature is examined.

The linearity of pressure and melt temperature for motor power steps of ± 2 , ± 4 , ± 6 , and ± 8 for polymer DFDQ was investigated at a mean operating level of approximately 50 r/min. Process gains were determined by averaging the results obtained after the responses reached steady state. The results indicate that the gains, 98 kPa/M.P. for pressure and 0.2°C/M.P. for temperature, are linear within this region. The linearity results and the gains are consistent with similar results presented by Kochhar and Parnaby (6).

The midpoint of the extruder screw speed operation is quite linear; however, this linear region becomes reduced as one reaches the upper levels of operation. As discussed previously, a step from 74 to 80 M.P. results in process gains of 76 kPa/M.P. and 0.19°C/M.P., whereas a step from 80 to 86 M.P. gives gains of 32 kPa/M.P. and 0.09°C/M.P. The change is quite significant for this relatively small range of operation. As a result, not only would any controller parameters determined for midrange operation have to be modified for operation at upper levels but the nonlinearity in this upper level of operation will necessitate detuning the controllers in order to maintain system stability. One might expect that changes in polymer quality would also necessitate retuning the controllers.

Because commercial polymers may have varying characteristics from batch to batch, it was decided to study the effect of polymer quality on the extruder per-

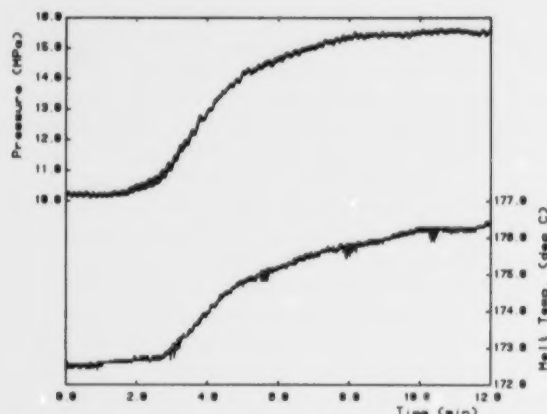


Fig. 8. Step responses of melt pressure and temperature to polymer feed quality changes.

formance. As a gross approximation to this phenomenon, a step change in polymer feed type was introduced to the extruder. Figure 8 shows the results of a change from DFDQ to DFDY polymers. As can be seen in Table 1, the melt indices of the two polymers are very different, resulting in a large disturbance. The pressure increased from 10.1 MPa to 15.7 MPa, with a corresponding temperature increase of 5°C. By contrast a typical change of 8.0 in motor power with DFDQ will yield 1.0 MPa and 1.6°C changes. The shape of the disturbance response appears to be second order, as was also observed by Schott (13) in similar experiments.

Introducing a step change in polymer type with two polymers with smaller property differences will yield a similarly shaped response, although the magnitude of the changes in temperature and pressure will be reduced.

The experimental results presented here generally agree with literature results. The only exception is the response of the pressure as the temperature increased during a step change in screw speed. Fingerle (4) and Fontaine (14) reported that the pressure drifted downward as the temperature increased. This drift was not observed in the steps presented here. However, it is possible that a small downward drift was masked by the large pressure surges. In general, variations in the mean level of the pressure were observed as the melt temperature changed, especially during startup conditions.

The step test experiments match the simulation results of Tadmor, *et al.* (15), except that their simulated temperature response has an overshoot, and the experimental pressure response does not drift downward as the temperature increases. The simulation results of Brauner, *et al.* (2), do not resemble the experimental change in polymer quality. Their simulation shows a sharp change in pressure at the die when the new polymer reaches that section of the extruder, in contrast with the second-order response observed here. It would appear that the simulation does not account for any mixing of the polymers, either in the hopper or as they melt in the extruder. This might possibly account for the discrepancy between the model and the current experiments.

TIME-SERIES MODELING

In the previous section, it was shown that the transfer function for screw speed to pressure can be modeled adequately by a first-order model with a very small time constant. Looking at a response such as Fig. 7, one can see that the disturbances caused by the pressure surging can be almost as large as those caused by a step of six units in the motor power. The data in Figs. 2 and 6 also show significant pressure variations. When the process disturbances are such a large part of the overall process behavior, it is very important that they be modeled so that one can then determine the most effective control strategy to eliminate these disturbances.

A serious defect in classical modeling techniques is that the noise is neglected. Both Fontaine (14) and Wright (16) observed large pressure fluctuations; however, both chose to ignore this information. Fontaine modeled only the long-term pressure level, and Wright performed setpoint changes in desired screw speed without attempting to regulate the pressure.

The time-series modeling approach (Box and Jenkins (10)) develops both a transfer function and a noise model. The noise model can then be used to predict the next value of the disturbance allowing for improved control. Sometimes, it is possible to obtain many models of the process with comparable fits (especially when only a small amount of data are used). Selecting the best form of the model should depend upon process knowledge. Some of the models presented by Kochhar and Parnaby (6) were inadequate from this point of view. An analysis of their model is presented by Costin, *et al.* (1).

For this work, a PRBS signal was input to the extruder motor controller at 0.5 s intervals. The extruder produced DNDY polymer operating at a mean level of approximately 49 r/min, with the motor power alternating by ± 1 about the mean value. The sequence frequency was selected so that a reasonable dynamic model could be identified without unduly straining the extruder motor while allowing the possibility of controlling against the disturbances already observed in the system. In order to capture detailed information about the flight noise, the system was sampled at a higher frequency (4.0 Hz) than the control input. Models for control purposes used data points corresponding to the times of input signals.

The data were modeled by Eq 5,

$$\nabla_s P_t = \frac{\omega_0(1 - \omega_x z^{-x} - \omega_{x+1} z^{-x-1})}{(1 - \delta z^{-1})} U_{t-1} + \frac{(1 - \theta_1 z^{-1} - \theta_2 z^{-2})}{(1 - \varphi_1 z^{-1} - \varphi_2 z^{-2})} a_t \quad (5)$$

where the parameters and their 95 percent confidence bands are:

$$\begin{aligned} \omega_0 &= 70.7 \pm 3.4 \text{ kPa/motor power} \\ \omega_x &= 0.711 \pm 0.064 \\ \omega_{x+1} &= 0.521 \pm 0.065 \\ \delta &= 0.281 \pm 0.039 \\ \theta_1 &= 1.134 \pm 0.154 \\ \theta_2 &= -0.295 \pm 0.163 \\ \varphi_1 &= 1.722 \pm 0.079 \end{aligned}$$

$$\begin{aligned} \varphi_2 &= -0.869 \pm 0.079 \\ \nabla_s &= 1 - z^{-s} \\ s &= 60/\text{TACH}_t/T_s \quad (\text{TACH}_t \text{ is in r/min}) \\ T_s &= \text{sampling time} = 0.5 \text{ s.} \\ x &= \text{integer truncation of } s \end{aligned}$$

The flight noise has a period solely dependent upon the screw speed ($60/\text{TACH}_t$ s). This noise can be modeled as a seasonal nonstationarity denoted by a ∇_s term in the denominator of the noise model, where s is the number of lags corresponding to the period of the noise. Equation 5 is modeled with the ∇_s term multiplying P_t which, in fact, provides the seasonal (periodic) differencing required to show the flight noise effect on pressure. As a result, the $(1 - \omega_x z^{-x} - \omega_{x+1} z^{-x-1})$ term arises in the numerator of the transfer function term, where it provides a low-order expansion approximation to ∇_s . Because $60/\text{TACH}_t/T_s$ can have noninteger values, the ∇_s term was physically implemented by linearly interpolating between the sampled data, which were 0.25 s apart. The term $(\omega_x z^{-x} + \omega_{x+1} z^{-x-1})$ weights the input signals at values of x lags and $x + 1$ lags, acting like a linear interpolator, although a surprising result was that the sum $(\omega_x + \omega_{x+1}) = 1.232$, determined by the fitting routine, significantly exceeds the expected value of 1.0. Model inaccuracies and the low-order approximation probably account for this error.

If one rewrites Eq 5 in terms of P_t and assumes that the ∇_s term cancels its approximation in the numerator of the transfer function, one can analyze each term of the model to determine its physical significance.

Box and Jenkins (10) give equations relating a first-order transfer function model to a continuous system. The system time constant is given by

$$\tau/T_s = -1/(\ln \delta)$$

For the values in Eq 5, $\tau = 0.39$ seconds. The process gain is calculated by replacing z^{-1} with 1.0 in the transfer function term and by collecting the constants to give $g = 121$ kPa/M.P. (The terms $(1 - \omega_x z^{-x} - \omega_{x+1} z^{-x-1})$ are neglected in this calculation because they cancel the ∇_s term).

The noise model is an ARMA (2, 2) (second order in both denominator and numerator of the noise model). An AR (2) (second order in the denominator) will model a damped sinusoidal behavior when its roots are imaginary ($\varphi_1^2 + 4\varphi_2 < 0$), as is the case for Eq 5. Box and Jenkins give the frequency and damping factors as:

$$\begin{aligned} \zeta &= \sqrt{-\varphi_2} \\ f_0 &= 2\pi T_s \cos^{-1} \frac{|\varphi_1|}{2\sqrt{\varphi_2}} \end{aligned}$$

For the denominator of the noise portion of Eq 5, the damping factor is 0.93 and the frequency is 0.125 Hz (period of 8.0 s).

The time series model is in good agreement with the parameters for the gain (121 kPa/M.P. versus 110 kPa/M.P.), time constant (0.39 s vs. 0.2 s), and surging period (8.0 s for both) approximated from the steady-state and step-test analysis given in the previous section.

DIGITAL PROPORTIONAL—INTEGRAL CONTROL

There have been many attempts in the literature to construct dynamic models between melt pressure as output and screw speed manipulations as input. However, very few of the authors have tested their models or control schemes by attempting to regulate an actual extruder. Dormeier (17) briefly describes an analog control system, similar to the analog pressure controller on the extruder used in the experiments for this work, and Hassan and Parnaby (11) used PID controllers whose setpoints were computed from a steady-state, linearized model of the extruder. However, all other authors stopped in the modeling stage and did not implement their recommended control schemes. The objective of this control study was to reduce the pressure variations in the extruder. Digital PI and self-tuning regulators were used and compared with open-loop, steady-state extruder behavior.

The previous two sections discussed the modeling of the extrusion process. In particular, the most significant noise is divided into two categories. The first category consisted of a pressure surging with an 8-s period due to the breakup of the extruder solid zone. The second category was a signal noise caused by the screw flight passing the tip of the pressure transducer. This section describes the first attempt to control an extruder for pressure surging, while the pressure signal is affected by flight noise.

The first control algorithm applied on the extruder was a digital PI algorithm. This was used as the simplest case that might be used commercially. The algorithm implemented was the velocity form of the digital PI algorithm, Eq 6 (Smith (18)).

$$U_t - U_{t-1} = \nabla U_t = K_c((e_t - e_{t-1}) + T_I/T_e e_t)$$

where

$$e_t = P_{set} - P_t \quad (6)$$

The tuning parameters K_c and T_I were tuned on-line by trial and error.

Figure 9 shows a typical example of the control action and pressure response of a digital PI controller applied on the extruder. The control and sampling rates were kept constant at 2 Hz throughout the experiment. No control was taken during the first 5 min. The PI controller was then started with initial tuning parameters,

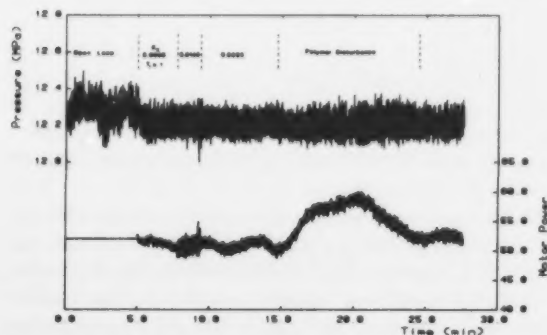


Fig. 9. Digital PI control of pressure: unfiltered data.

$K_c = 5.8 \cdot 10^{-3}$ M.P./kPa and $T_I = 1.0$ s. Following this, the controller was tuned for elimination of the 8-s surging, with the final control parameters selected as $K_c = 8.7 \cdot 10^{-3}$ M.P./kPa and $T_I = 1.0$ s. The parameter tuning results in other similar runs varied as much as ± 100 percent about the above values, showing some drift in the process.

The controller algorithm was tested for its effectiveness in the face of both the pressure surges and a disturbance in product quality. The product quality disturbance consisted of a pulse change in polymer from DNDY to DFDQ. As can be seen in Fig. 9, the controller completely eliminated any offsets or long-term drifts. The second-order response to the change in polymer has been eliminated. Looking at the controller action, one can see that any drifts or cycles in pressure have, under closed loop conditions, become drifts or cycles in the manipulated variable.

The control objective is to regulate the pressure against both the pressure surging and a disturbance in product quality. It is also desired that the controller take as little action as possible in response to the signal noise caused by the screw flight. However, because the flight noise is large relative to the surging and is at a higher frequency, no control setting was found that eliminated the 8-s surges without taking control action based on the signal noise. In most cases, the flight noise was amplified by the controller.

The controller was very effective in eliminating any long-term drifts and the changing polymer disturbance. However, the algorithm was much less successful in eliminating the 8-s surging. The high-frequency control actions concentrate almost exclusively on the flight noise. This can be observed more clearly in Fig. 10. This figure shows the pressure data given in Fig. 9 digitally filtered off-line by an eighth-order Butterworth low-pass filter with a cut-off frequency of 1/3 Hz. The high-frequency pressure signal is an artifact of the pressure measurement, and only the lower frequencies of the pressure data show the true effect that the controller has upon the product quality. In the remaining figures, only off-line filtered data will be shown. This filtering removes the high-frequency pressure components. In Fig. 10, the PI controller has removed the offset and the longer-term cycling. However, the 8-s surging has only been partially removed. The amplitude appears to be approximately half that of the open loop value. The con-

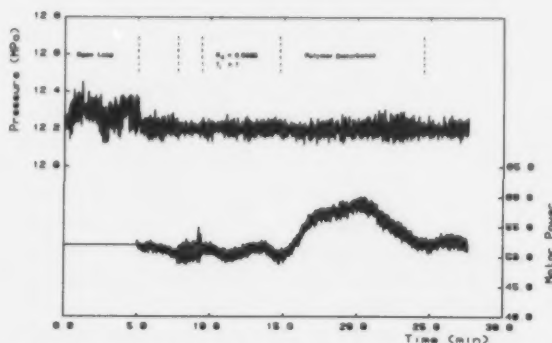


Fig. 10. Digital PI control of pressure: off-line filtered data.

control deteriorated during the polymer disturbance. The variance of the pressure increased by 20 percent, as compared to the controlled data before the disturbance. These variances are calculated for a number of sequences of data, each 150 samples long. The increased variance was due to the process changing as the extruder moved to a new operating level which, in turn, would require a different noise model and transfer function. Under these conditions, the PI controller would require new parameter settings. The objective of these runs was to find a controller that needed minimum attention by plant personnel. Therefore, the controllers, in this and subsequent experiments, were not retuned during a polymer-quality disturbance. The experiments provide an extreme test for robustness of the controllers under various ranges of extruder operating conditions and for various polymer qualities.

DIGITAL PI CONTROL WITH ON-LINE FILTERING

A number of digital bandstop filters were applied to the extruder pressure measurements in an attempt to remove the flight noise, thereby making the controller more effective in reducing the inherent pressure surging. These filters and their effect on closed-loop control are discussed in detail by Costin (19). In general, it is shown that these filters added too much phase lag to the system for effective control. The most effective bandstop filter used was constructed by a transfer function consisting of 2 poles and 2 zeroes, given by Eq 7:

$$H(s) = \frac{(s + \sqrt{ab})^2}{(s + a)(s + b)} \quad (7)$$

where b and a are the upper and lower cutoff frequencies in rad/s. This filter has maximum and minimum phase shifts of $\pm 90^\circ$, respectively. If one does not worry about nonunity amplitude in the high-frequency section, one can construct narrower bandstop filters by replacing the $\sqrt{ab}$ term in Eq 7 with c ; c is the center frequency of the filter, allowing another degree of freedom in specifying the filter. These types of filters are similar to the lead-lag compensators commonly used by electrical engineers.

For the extruder system, removal of the flight noise from the pressure signal requires a narrow stop band (corresponding to 20 r/min to 90 r/min, the operating region of the extruder) and the following parameters were chosen: $a = 0.3$ Hz, $b = 1.5$ Hz, $c = 1.0$ Hz, and sample time = 50 ms. The amplitude ratio at 2.0 Hz, the control frequency, was 0.45. The filter was discretized using the Tustin bilinear transformation (Franklin and Powell (20)). The amplitude at 1.0 Hz was still large, 0.48, so the filter was cascaded with itself to give a filter: $H(s) = (s + c)^4 / ((s + a)^2 (s + b)^2)$. This gives an amplitude of 0.23 at 1.0 Hz. Because of the narrowness of the filter, the amplitude at 2.0 Hz is only 0.20. Figure 11 shows the control results for the PI algorithm in combination with the cascaded 2 pole/2 zero filter.

Comparing the pressure data of Fig. 11 to those of Fig. 10 shows that the inclusion of the 2 pole/2 zero filter in the control loop reduces the variance of this

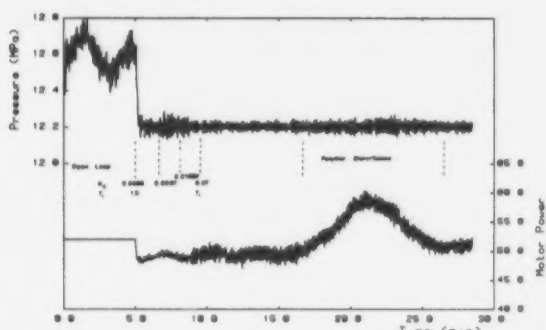


Fig. 11. Digital PI control of pressure: 2 pole/2 zero filter.

filtered pressure by 33 to 50 percent. The control parameters selected for best tuning in the 2 pole/2 zero case are $K_c = 1.885 \cdot 10^{-2}$ M.P./kPa and $T_i = 0.7$ s. These are much higher values than those allowed in the unfiltered pressure experiment, showing that the filter had significantly improved the controller's ability to perform. For both cases, however, the control deteriorates during the polymer disturbances.

Because of the narrowness of the filter and the resulting 80 percent attenuation at high frequencies, another filter was constructed using $a = 0.3$ Hz, $b = 3.0$ Hz, and $c = 1.0$ Hz. This filter was implemented with a control frequency of 4.0 Hz; a frequency outside the stop band of the filter. The amplitude at 4.0 Hz is 0.86, or 0.74 when the filter is cascaded with itself. The results for this filter cascaded with itself and PI control are shown in Fig. 12. The variance of this case was reduced by 20 to 40 percent over the previous 2 pole/2 zero filter; i.e., a reduction of from 55 to 90 percent over the unfiltered case. The final tuning parameters are $2.03 \cdot 10^{-2}$ M.P./kPa and 0.8 s, very close to those used in the previous case. Again, the control deteriorated during the polymer quality disturbance. The variances during this disturbance are about equal for Figs. 11 and 12.

Of all the filters used in combination with the PI algorithm, the data of Fig. 12 show the most success in regulation of the 8-s pressure surging. It is successful because the filter attenuates the flight noise without introducing an excessive amount of phase change into the system. The controller can then be tuned to reduce the 8-s surging, as opposed to the flight noise, without too much danger of destabilizing the system.

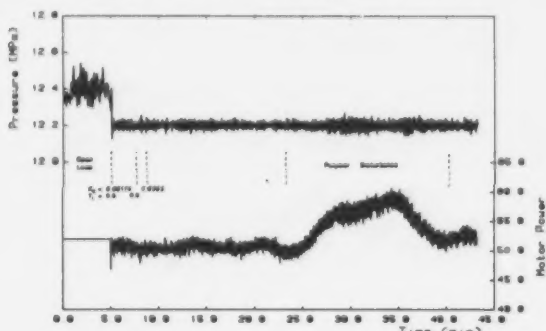


Fig. 12. Digital PI control of pressure: 2 pole/2 zero filter; control at 4 Hz.

One important point to note is that the filter has a considerable effect on the process model. This was examined by developing a time-series model for the process together with the 2 pole/2 zero filter. This model is given in Eq 8.

$$P_t = \frac{(\omega_0 + \omega_1 z^{-1} + \omega_2 z^{-2} + \omega_3 z^{-3})}{(1 - \delta_1 z^{-1} - \delta_2 z^{-2} - \delta_3 z^{-3} - \delta_4 z^{-4})} U_{t-1} + \frac{(1 - \theta_1 z^{-1} - \theta_2 z^{-2} - \theta_3 z^{-3})}{V(1 - \varphi_1 z^{-1} - \varphi_2 z^{-2} - \varphi_3 z^{-3})} a_t \quad (8)$$

$$\omega_0 = 11.4 \pm 2.4 \text{ kPa/M.P.}$$

$$\omega_1 = 43.2 \pm 5.0 \text{ kPa/M.P.}$$

$$\omega_2 = 61.9 \pm 5.8 \text{ kPa/M.P.}$$

$$\omega_3 = 27.7 \pm 3.2 \text{ kPa/M.P.}$$

$$\delta_1 = -0.818 \pm 0.072$$

$$\delta_2 = 0.279 \pm 0.095$$

$$\delta_3 = 0.314 \pm 0.082$$

$$\delta_4 = -0.318 \pm 0.07$$

$$\theta_1 = 0.548 \pm 0.176$$

$$\theta_2 = -0.397 \pm 0.129$$

$$\theta_3 = 0.569 \pm 0.067$$

$$\varphi_1 = 0.679 \pm 0.159$$

$$\varphi_2 = -0.258 \pm 0.165$$

$$\varphi_3 = 0.075 \pm 0.158$$

This is quite a complex model in which the transfer function has more parameters than the transfer function in Eq 5. Even with the large number of parameters in Eq 8, there are still a few significant lags in the auto- and partial-auto correlations of the residuals, indicating that even more parameters would be needed in the noise model to reduce the fitting residuals to pure white noise. However, Eq 8 should represent the system fairly accurately (the transfer function portion is a very good fit) and is sufficient to study the effect of the filter on the system.

A comparison of Eqs 8 and 5 shows the vast difference between the process alone and the process including the filter. The first-order system of Eq 5, considered without the flight noise, would be much easier to control than the nonminimum phase system of model (8). This is why the PI controller cannot totally eliminate the 8-s surging.

Figure 13 shows the melt temperature response for the data of Fig. 11. The die-wall temperature is always under regulation by the die analog PI temperature con-

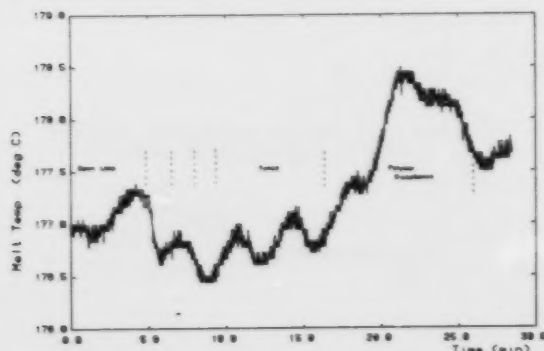


Fig. 13. Temperature response data for the exponent of Fig. 11.

troller. However, as shown in Fig. 5, this controller is not regulating the melt temperature property, causing cycling with a 1.5 min period. When the new polymer impulse enters the system, the melt temperature follows the control action to a new operating level. It returns to a point slightly above its former level with the return of the old polymer. The die temperature controller is not able to maintain the melt temperature at a constant operating level.

SELF-TUNING AND MINIMUM-VARIANCE CONTROL THEORY FOR THE PLASTICATING EXTRUDER

After using the PI algorithm to control the extruder pressure, a self-tuning regulator (STR) algorithm was implemented to control the same process. Recall that the PI algorithm was only able to compensate partially for the 8-s surging and that control deteriorated as a polymer disturbance entered the system. It was expected that the STR would give improved control due to its optimal structure and its ability to change the controller parameters in order to compensate for changing process conditions. The self-tuning algorithm has been presented by many authors (i.e., Borison and Syding (21) and Harris, *et al.* (22)). The control action is calculated by Eq 9.

$$\nabla U_t = - \frac{(\alpha_0 + \alpha_1 z^{-1} + \dots + \alpha_m z^{-m})}{(\beta_0 + \beta_1 z^{-1} + \dots + \beta_l z^{-l})} Y_t \quad (9)$$

where ∇U_t is the change in Motor Power and Y_t is the measured pressure.

The parameters ($\alpha_0 \dots \alpha_m, \beta_0 \dots \beta_l$) are determined by the discounted recursive least-squares algorithm, Eq 10.

$$\begin{aligned} \theta_{t+1} &= \theta_t + K_t [Y_t - \beta_0 \nabla U_{t-1} + \xi \nabla U_{t-1} - \psi_{t-1}^T \theta_t] \\ K_t &= \underline{C}_t \psi_{t-1}^T [\lambda + \psi_{t-1}^T \underline{C}_t \psi_{t-1}^T]^{-1} \end{aligned} \quad (10)$$

$$\underline{C}_{t+1} = \{\underline{C}_t - K_t [\lambda + \psi_{t-1}^T \underline{C}_t \psi_{t-1}^T] K_t^T\} / \lambda$$

where

$$\begin{aligned} \theta_t &= [\alpha_0 \alpha_1 \dots \alpha_m \beta_1 \beta_2 \dots \beta_l]^T \\ \psi_t &= [Y_{t-1} \dots Y_{t-m} \nabla U_{t-1} \dots \nabla U_{t-l}]^T \\ \underline{C}_t &\text{ is the normalized covariance matrix of the parameter estimates} \end{aligned}$$

K_t is a vector weighing the error at time t , and θ_t is the vector of calculated parameters.

The tuning parameter λ is a forgetting factor for past data. The asymptotic window length or the effective number of observations used in the estimation routine is given by $(1 - \lambda)^{-1}$. The range of $0.95 \leq \lambda \leq 1$ is usually chosen, which gives effective window lengths ranging from 20 samples to infinity (there is no discounting of past values for $\lambda = 1$).

The ξ in Eq 10 is a constraining factor weighting the past control actions. A value of $\xi = 0$ will tune controller Eq 9 to the minimum variance control equation, provided the structures (the values of m and l) are correct. The constraining factor is generally very effective in reducing the variance of the manipulated variable with-

out significantly increasing the variance of the controlled variable. It is especially useful for nonminimum phase systems, which have unstable minimum variance (M.V.) controllers but which can be stabilized by imposing constraints on the algorithms.

Generally, the values of m and l are chosen from the minimum variance control structure. This can be most easily demonstrated through an example. Taking the time series model developed in Eq 5 and rewriting it to include the ∇_s term in the noise model (along with the $(1 - \omega_x z^{-x} - \omega_{x+1} z^{-x-1})$ term, which cancels the ∇_s factor), we obtain:

$$P_t = \frac{\omega_0}{(1 - \delta z^{-1})} U_{t-1} + \frac{(1 - \theta_1 z^{-1} - \theta_2 z^{-2})}{(1 - \varphi_1 z^{-1} - \varphi_2 z^{-2}) \nabla_s} a_t \quad (11)$$

The ∇_s term models the flight noise. Normally this nonstationary term would be compensated by a nonstationary control action. However, it is desired that the controller not take action based on the flight noise. Additionally, in most cases, the flight noise will be removed by a filter eliminating the need for the ∇_s term in the model. Therefore, the ∇_s term was replaced in the model by one of its roots, $\nabla = (1 - z^{-1})$, the difference operator. The ∇ term forces the minimum variance controller to include integral action, which eliminates any offsets or level changes in the process. Equation 11 becomes Eq 12:

$$P_t = \frac{\omega_0}{(1 - \delta z^{-1})} U_{t-1} + \frac{(1 - \theta_1 z^{-1} - \theta_2 z^{-2})}{(1 - \varphi_1 z^{-1} - \varphi_2 z^{-2}) \nabla} a_t \quad (12)$$

Following procedures outlined by Box and Jenkins (10) and using values for the parameters from Eq 5, the minimum variance controller becomes:

$$\nabla U_t = \frac{-(1.588 - 2.742z^{-1} + 1.514z^{-2} - 0.244z^{-3})}{70.7(1 - 1.722z^{-1} + 0.869z^{-2})} P_t \quad (13)$$

The $(1 - \varphi_1 z^{-1} + \varphi_2 z^{-2})$ term in Eq 12, forces the controller, Eq 13, to take control action matching the 8-s surging. Equation 13 also includes terms for the inverse of the plant dynamics and for the prediction for the noise model. This unconstrained controller attempts to compensate for any disturbances in one sampling period.

Normally, the orders for m and l for the STR would be selected from the M.V. controller, Eq 13, as $m = 3$ and $l = 2$. However, because of the relatively small value of the term $a_3 = -0.244$, the order of m was selected as $m = 2$, to simplify the calculations. Initial guesses for the STR parameters can also be taken from Eq 13.

In much of the literature on the STR algorithm, there is controversy as to whether the β_0 parameter of Eq 9 should be constant. Poor guesses of a fixed β_0 can cause problems of system stability and poor convergence. However, if β_0 is being estimated, poor behavior in the algorithm (such as momentary "bursts" in the parameter values) can occur when the parameters converge. The usual practice is to estimate β_0 until the parameters converge and then to hold it constant at this value. For the

STR used in this work, β_0 was fixed, mainly to simplify the calculations by reducing the matrix sizes and the computation time. The value of β_0 was taken as $(\omega_0 + \xi)$, which is a good estimate that would avoid any problems of stability or convergence.

SELF-TUNING REGULATOR RESULTS

The self-tuner theory presented in the previous section was implemented on the extruder to compare its performance to that of the digital PI algorithm. It was hoped that the larger structure and the parameter following characteristics of the STR would yield improved control over the PI cases.

For completeness, the STR was implemented with a 0.5-s control interval and using unfiltered pressure data as the input signal. Figure 12 shows the pressure data and control action for this run. The 8-s surging is quite noticeable, with a variance comparable to that of Fig. 10 but considerably higher than the PI algorithm in combination with the 2 pole/2 zero filters, Figs. 11 and 12. The unfiltered STR achieved comparable results to the unfiltered PI but takes considerably larger control actions. This means that the extruder motor is doing more work, with greater electrical usage and more wear on the moving parts, for the same level of control. As is the case for the unfiltered PI controller, the STR is taking control action on the flight noise, thereby not effectively regulating the 8-s surging. The STR tunes itself to eliminate the signal noise, which is seen as the most significant disturbance.

A typical STR controller for the unfiltered data, found by taking representative parameter settings, is given by Eq 14:

$$\nabla U_t = \frac{-(0.625 + z^{-1})}{76(1 + 1.59z^{-1} + 0.9z^{-2})} P_t \quad (14)$$

Analysis of Eq 14 shows that the STR has tuned its poles into a controller that regulates against a sinusoid of frequency 0.186 Hz coupled with the flight noise. This results from the STR tuning its parameters to compromise between the 8-s surging, the flight noise, and the level of constraining of the controller. The final controller is ineffective in regulating either the flight noise or the surging. Although this tuning is the expected result, the desired action would be that the STR ignore the flight noise, adapting instead only to the 8-s surging in the system.

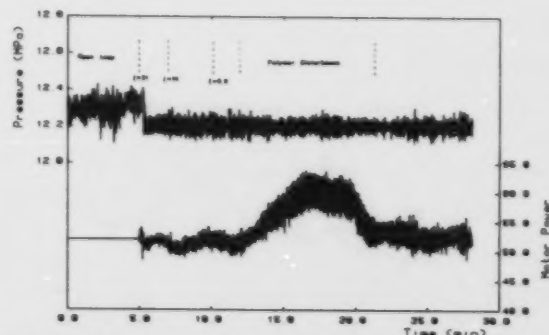


Fig. 14. Self-tuning regulator control of pressure.

At a sampling frequency of 2.0 Hz, the flight noise, which lies between 0.8 Hz and 1.0 Hz (for 50 to 60 r/min), is close to the Nyquist frequency of 1.0 Hz. The STR would have difficulty identifying the flight noise at these frequencies and, therefore, the constraining factor can be relatively low. In order to study this effect, an STR with a control frequency of 4.0 Hz was implemented. This case needed a very high constraining factor (75.8 kPa/M.P.), in contrast with 6.9 kPa/M.P. for the previous case. The parameters were tuned by the STR to become equivalent to a gain term, reducing the algorithm to an integral controller. The STR has determined that almost all the disturbance corresponds to the high-frequency-signal noise, and this it tries to compensate for with equally fast control actions.

Figure 15 shows the results for the STR with a control frequency of 2 Hz and the twin cascaded 2 pole/2 zero filter previously used for the experiment, shown in Fig. 11. The variances were equivalent to the PI algorithm results. During the change in polymer, the algorithm allowed a small amount of offset from the setpoint pressure. The control action taken during the polymer disturbance was more extreme under STR control than under PI control. In addition, when first initiated, the STR became unstable. It was quickly stabilized by increasing the constraining factor.

The plot of the parameters determined by the STR is presented in Fig. 16a and b. After the initial tuning period, the parameter values converge to a controller approximated by $\nabla U_t = -(2.9 + 0.0z^{-1} + 0.0z^{-2}) P/(91.0(1.0 + 0.8z^{-1} + 0.8z^{-2}))$. The numerator is reduced to a gain term, and the denominator models a damped sinusoid with a frequency of 0.35 Hz. This is very close to the frequencies that appear in the noise portion of the time-series model, Eq 8, and the lower-corner frequency (0.3 Hz) of the filter. The poor response of this controller-filter combination is due to the STR trying to compensate for the filter.

During the polymer disturbance in which the extruder has moved to a new operations level, the STR parameters changed considerably. In combination with the filter, this new operating level may have a considerably different time-series model, meaning that the STR would tune to a very different controller. This ability to follow the changing process parameters should

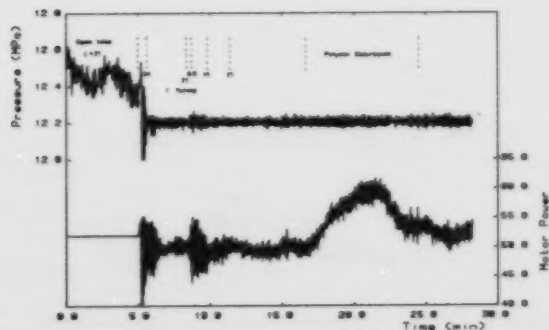


Fig. 15. Self-tuning regulator control of pressure: 2 pole/2 zero filter.

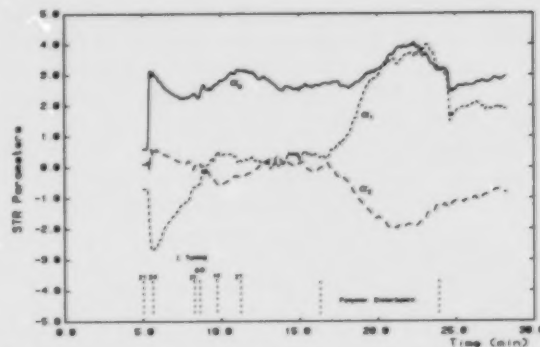


Fig. 16a. STR α controller parameters for the experiment of Fig. 15.

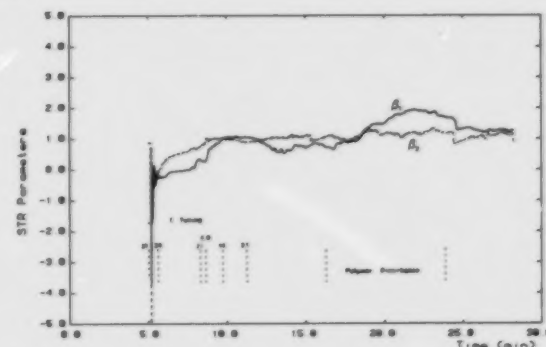


Fig. 16b. STR β controller parameters for the experiment of Fig. 15.

mean that the STR would give improved control over the fixed parameter PI controller. However, the performance of the STR, as compared to the digital PI algorithm, was disappointing. There was no noticeable improvement in pressure control by the STR over the digital PI controller. At first glance, this is a surprising result. The larger structure and parameter updating characteristics of the STR should provide superior control. However, one must remember that the STR will tune itself, depending on the disturbances and noise present, in accordance with the type of controller structure used. What part or which frequency of the noise structure that the STR is compensating was discussed for the experiments reported in this paper. In each case, the STR is doing a good job controlling the parts of the process that it identifies as the most important. However, it is not desired that the STR regulates the flight noise or compensates for a filter. The STR defeats the use of bandstop filters by identifying the dynamics of the filter and by trying to invert these dynamics in the controller, eliminating most of the advantage originally gained by filtering. The controller is not allowed to tune to the desired control equation that would control the real 8-s disturbance.

SUMMARY AND CONCLUSIONS

This paper presents the interfacing, modeling, and control of a plasticating extruder using a minicomputer control system. The regulation of extruder pressure is studied by using the screw speed as a manipulated variable. Steady-state information, step tests, and time-

series analysis are used to develop dynamic models for the transfer function between screw speed and pressure and also to model the disturbances associated with the extruder pressure.

The pressure-time constant is found to be very rapid, approximately 0.4 s. The disturbances of the melt pressure were found to consist of long-term oscillations with a 3.0-min period and pressure surging with a period of 8-s due to the periodic breaking up of the tip of the solid region. Signal noise at the same frequency as the screw rotation was also observed. This is due to the screw flight passing the tip of the pressure transducer.

A time-series model for the process is presented in Eq 5. This model is an improvement over previous models presented in the literature. It identifies the system-time constant and the frequencies of the main system disturbances very accurately. The transfer function relating pressure to screw speed is a first-order model. The noise model has terms modeling both the extruder-pressure surging and the flight noise.

In order to approximate small disturbances in polymer quality, the extruder was switched from one type of polymer to another by introducing the new polymer into the extruder hopper. This change caused a second-order response in pressure and temperature.

Digital PI and self-tuning regulator algorithms were implemented on the extruder to regulate the pressure. As expected, both controllers were able to successfully control for long-term drifts in the pressure level and a disturbance caused by a change in polymer quality. If one is interested in the long-term regulation of the extruder pressure, it is recommended that any surging or flight noise information be removed by low-pass filtering.

For the case where flight noise is not present in the extruder, it is recommended that a self-tuning regulator, using the structure of Eq 13, be used to regulate the pressure. No signal noise would be present if the pressure transducer is situated in the die or the adapter region of the screw.

Various filters were used to eliminate the signal noise. However, the filter substantially changed the process-transfer function. This affected the ability of the controllers to regulate the process. The combination of controller and filter that was found to be best able to control the process was the digital PI algorithm with a twin-cascaded 2 pole/2 zero filter.

The STR was found to be comparable to the PI controller. This unexpected result is due to the self-tuning regulator tuning itself to compensate for a filter in the loop or the flight noise and not for the elimination of the process disturbances. Experiments showed the poor control results achieved by the STR algorithm when it is used with filters that have dynamics that are comparable to the sampling frequency.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the Natural Sciences and Engineering Research Council of Canada for supporting the research described in this article through Grants No. A6075 and A7017. All the polymer

used in this project was donated by Union Carbide of Canada and is gratefully acknowledged.

NOMENCLATURE

a, b, c	= parameters
a_i	= white noise series
$\underline{C}$	= normalized covariance matrix of parameter estimates
e_i	= error signal
f	= number of periods of delay
f_0	= frequency
g	= process gain
$H(s)$	= filter transfer function
K	= vector weighing past parameters and present errors in controlled variables
K_c	= PI controller gain
l	= order of the STR denominator polynomial
m	= order of the STR numerator polynomial
P	= pressure
P_{SET}	= pressure setpoint
s	= Laplace transform variable; also period in seasonal filter operator
T	= melt temperature
T_i	= PI controller integral action
T_s	= sampling time
$TACH_i$	= screw speed at time i (rev/min)
t	= subscript time for discrete variables
U	= control action
x	= integer part of seasonal operator, s
z	= Z-transform variable
α	= parameter in STR algorithm
β	= parameter in STR algorithm
∇	= difference operator $(1 - z^{-1})$
∇_s	= seasonal difference operator $(1 - z^{-s})$
$\delta(z^{-1})$	= polynomial in time series transfer function representing system dynamic terms
θ	= vector of parameters
$\theta(z^{-1})$	= moving average terms of noise model
λ	= forgetting factor, STR algorithm
ζ	= damping factor
ξ	= constraining factor, STR algorithm
τ	= time constant
$\varphi(z^{-1})$	= autoregressive term of noise model
ψ	= vector of past control actions and controlled variable
$\omega(z^{-1})$	= polynomial in time series transfer function representing system zeroes

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Discussion of J. D. Wright Article

M. R. Kamal. It seems that, in order to control a certain variable (like pressure) and to smooth out the output, you had to sacrifice control over something else, probably temperature. Is this correct?

J. D. Wright. No. We have a multi-variable system in effect; the temperature and pressure both move substantially with different time constants. The pressure fluctuates rather rapidly, temperature less so because the time constants are much larger. The two interact a great deal, and if, for example, you increase the temperature, the viscosity is reduced and the pressure drops.

In order to solve the pressure problem, we attempted to control the temperature with the die temperature controller, but this did not work well. What we sacrificed was a rather extensive manipulation of screw speed; in order to control the pressure and the temperature, one manipulates the screw speed. The problem is that, unless one is careful, there is the danger of burning out the controller motor on the screw.

M. R. Kamal. How did this ultimately affect flow rate when screw speed changes to that extent?

J. D. Wright. The flow rate stayed constant, inasmuch as the pressure was constant. By reducing the variance on the pressure, and assuming that temperature remained reasonably constant, we minimized or reduced the variance on the thickness or the throughput, according to the standard relationships.

W. I. Patterson. You said that you had a nonstationary eight-seconds surging response. To have a nonstationary response means that you have an accumulation in the mass flow, and I do not see where you are accumulating polymer.

J. D. Wright. The term stationary is used in the control sense. What it really means is slow drifts up and down on the pressure trace with a period of eight seconds due to periodic breaking up of the solids. We approximated the cycling with the ∇ -term, which is just one delay term, and that effectively assumes that there is a nonstationarity. This is just a mathematical nicety that guarantees a proportional integral controller.

W. I. Patterson. In that case, would not the bandpass filter do the same thing? The bandpass is just allowing the eight-second frequency band to get through, and you are taking off both the low-frequency and high-frequency effects.

J. D. Wright. We cut out the high frequency with the bandpass filter but passed the eight-second and the three-minute.

Editor's Note

The following eight articles were presented during the second mini-symposium on polymer blends, "Polyblends '82," organized and sponsored by the Industrial Materials Research Institute of the National Research Council of Canada. The symposium took place on April 20th, 1982, at the Institute's location in Montreal.

"Polyblends '82" was the fifth symposium on plastics and processing organized by the Institute. We established the following calendar for these meetings: February—mathematical modeling, simulation, and control; April—polymer blends and alloys; and November—composites. Due to the generosity of Professor Roger S. Porter, we have the privilege of publishing the proceedings of these symposia in *Polymer Engineering and Science*.

The aim of this series of mini-symposia is primarily to serve as a thematic information exchange system. It is our belief that the three basic subjects of the meetings are going to become the keys to the future development of the plastics industry. We want to promote R/D in these areas by acting as a focus, a center of excellence, a locus for contacts between the researchers from industry and academia, between the technical and manufacturing personnel in Canada.

For the stated reasons, in each of the meetings, we try to balance research and commercial interests and to provide not only the most recent research data, but also the background for these studies. The format adopted, 45-minute-long presentations by invited speakers with transcripts of the discussions, seems to work rather well. The meetings enjoy larger popularity than the physical constraints of the Institute can accommodate.

"Polyblends '82" had two basic themes: polymer/polymer miscibility and commercialization of polymer blends. These two themes reflect the current trends in the field. An absence of the configurational entropy of mixing in polymer/polymer systems forces the researchers to look for specific mechanisms of macromolecular interaction. The studies, exciting from the fundamental point of view, bring a promise of new and better methods of compatibilization and alloying of polymer blends and, thus, improvement of quality of the finished product. The translation of the basic knowledge to a commercially viable venture poses a different, but neither easier nor less important, problem. The second group of articles, presented during the later part of the mini-symposium, deals directly with some of the issues. These, (in a sense, "how to" articles) should be of value to all interested in developing their own blends.

L. A. Utracki,
Guest Editor

Opening Remarks

Being the materials science division of the National Research Council of Canada, here at the Industrial Materials Research Institute (IMRI), we feel an obligation to promote the practice of our discipline by the industrial and scientific communities. We want to do so, not only within Canada, but in close cooperation with our academic colleagues abroad.

One of the ways to do that is to provide a forum for fruitful discussions where we can review recent advances, identify areas and problems meriting further investigation, and debate our differences. These forums also give us an opportunity to maintain a listening post and, thus, to determine the direction of our future work.

Our mini-symposia in polymeric materials correspond to the three main aspects of our own investigations: polymer blends, plastic composites, and mathematical modeling of forming processes. Concerning polymer blends and alloys, our First Mini-Symposium on Polymer Properties emphasized the thermodynamics of multiphase liquids. We followed this with the First Mini-Symposium on Polymer Blends, entitled "Polyblends '81," concentrating on miscibility, compatibility, and the relationship of properties to composition.

In today's mini-symposium, "Polyblends '82," we are attempting to dig a little deeper. We will be steering away from review papers toward discussing recent, specific accomplishments. Compatibility remains a concern. Dr. Porter and Dr. Eisenberg will tell us more on how to make the immiscible compatible. We will

then hear from Dr. St-Pierre and Dr. Kamal on some of their recent work. Dr. Prud'homme will talk to us about relaxation—relaxation properties of polymer blends that is—before we turn to morphologic aspects, listening to Dr. Frisch and to Dr. Plochocki.

It is nice to work with exotic blends of polymers of unusual structures giving us desirable properties—this helps us to understand the rules of the game, and these systems permit us to verify or reject our working hypotheses. Nevertheless, the usefulness of these properties is cost-dependent. We would like to work with the twenty or so polymers that are commercially produced on a large scale and can be produced at affordable prices. The unique industrial opportunity of polymer blends is their cost-effectiveness. When the extraordinary returns required on invested capital for new installations in today's inflation-ridden economy, it is not likely that we will see many new polymers mass-produced. But blends of existing resins offer a new technological frontier to us. Dr. Utracki will tell us more about this aspect.

Our last two symposia were published in their entirety in a separate issue of *Polymer Engineering and Science* (1). We hope that this prestigious journal will accord us the same honorable treatment for this mini-symposium.

I let you go to work, wishing you a good meeting and a lively discussion. The discussion is the best part of these symposia.

George L. Bata

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13C NMR Characterization of Intermolecular Interactions for Polymers. Part 3. Solvent Effect on the Blend Compatibility of Poly(Vinyl Methyl Ether) and Polystyrene

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The solvent has an influence on the homogeneity of the poly(vinyl methyl ether)-polystyrene, PVME-PS blends prepared by drying cosolutions. This influence has been analyzed in terms of the competition among polymer-polymer and polymer-solvent interactions. Model solutions have been prepared in which intermolecular interactions correspond to the interactions in this blend and in some of the cosolutions. These interactions in the model solutions have been detected and identified by applying Rummens' method. The ^{13}C NMR spectra have been determined for PVME and for styrene oligomer dissolved in n-alkanes, cyclohexane, diethyl ether, isopropyl methyl ether, diisopropyl ether, and chloroform, and for PVME dissolved in benzene, toluene, and cumene. The chemical shifts have been plotted against the parameter $g^2 = [(n_2^2 - 1)/(n_2^2 + 1)]^2$, where n_2 is the refractive index of the solvent. If the structural segment represented by certain carbon and some solvent has an interaction that is stronger than dispersive, the chemical shift for this carbon will deviate from the line formed by its shifts in n-alkane solutions. These deviations indicate characters and intensities of the intermolecular interactions. Results indicate that cyclohexane exhibits weak interactions with both of the polymers and does not interfere with their mutual interaction, leading to a compatible blend. Results also suggest that benzene and toluene interact in the PVME in the same manner as PS. This leads to a gradual increase of the number of polymer-polymer interactions as the concentration of the polymers is increased by solvent removal, resulting in a compatible blend. Chloroform apparently interacts more strongly with PVME than with PS but interacts strongly enough with both to restrict interaction among the two polymers. As the concentration of polymers in the cosolution is increased, PS forms a separate phase. This leads to an inhomogeneous blend when the solvent is evaporated.

INTRODUCTION

Poly(vinyl methyl ether), PVME, and polystyrene, PS, form compatible polymer blends from the cosolutions in tetrachloroethylene, benzene, toluene (1), and xylene (2). Those blends exhibit lower critical solution temperatures (2-5). Blends obtained from cosolutions in methylene chloride, chloroform, and trichloroethylene are inhomogeneous at room temperature (1, 2, 6). It has been reported that blends cast from trichloroethylene can be annealed to a homogeneous blend that exhibits both upper and lower critical solution temperatures (6).

The effect of the solvent on the compatibility of PS and PVME has been analyzed in terms of thermodynamic properties (4, 7, 8). To understand this complex relationship better, it would also be of interest to understand the specific intermolecular interactions, IMI, governing the compatibility on a molecular level.

In the course of the last several years, it was demonstrated that solvent-induced changes, SIS, in NMR chemical shifts may provide detailed information about the character of IMI (9-17). Based on such an analysis, the solubility of PVME in benzene has been attributed to the π -hydrogen bond between the electron-

deficient methoxy proton and π orbital in benzene. In addition, dispersive (van der Waals, London) interactions have been found between every C-H group in PVME and benzene (18). The same kinds of interactions are believed to lead to the compatibility of PVME and PS.

The aim of this work is to understand how the competition between the specific interactions affects the compatibility of the blends of PVME and PS prepared from the cosolutions. To attain this goal, an analysis of SIS has been applied to solutions of PVME in benzene, toluene, and cumene and to solutions of both polymers in n-alkanes, diethyl ether (DEE), isopropyl methyl ether (IPME), diisopropyl ether (DIPE), cyclohexane, and chloroform.

Background

A SIS (19) is a cumulative effect caused by nonbonding (20) and by both nonspecific (21) and specific (21) bonding IMI between the solute and solvent. A SIS caused by strong, specific IMI may be considered as being composed of two parts. One is the shift induced by the specific interaction and the second, by the simultaneous dispersive interaction (19, 21).

The dispersive interaction arises from coordination of charge fluctuation between neighboring molecules (22). It should have the same physical character for gasses and for solutions in nonpolar solvents (23, 24). Accordingly, chemical shifts observed in the gas phase and in solution in van der Waals solvents should be connected by some simple relation (9, 10, 25). Apparently, this relation was most successfully defined by Rummens (9-11). His experimental method is based on the theoretical finding that diamagnetic shielding of the nucleus depends on the square of the Onsager reaction field (23, 24, 26-29). In a modified Rummens approach (13-15), chemical shifts for a compound in van der Waals solutions are related as follows:

$$\delta = S_i \cdot g^2 + C \quad (1)$$

In this equation, $g^2 = [(n_2^2 - 1)/(n_2^2 + 1)]^2$, n_2 is the refractive index of the solvent, and S_i and C are constants, specific to each nucleus.

For a polar compound, the analysis of SIS is simplest if the compound can be dissolved in n-alkanes. Chemical shifts for the solute are plotted against g^2 for the corresponding solvent (Rummens plot). Shifts for solutions in n-alkanes form a straight line, called the Van der Waals line, VDWL. Shifts for solutions in other solvents are removed from the VDWL at their respective g^2 . Using this method, one can evaluate the effect of the IMI for every chemically, or sterically, different structural group that is distinguished in the NMR spectrum of a compound. The slope of the VDWL, S_i , reflects the tendency of this group to enter into dispersive interaction. It is influenced by the polarizability, ionization potential (10, 11), and (particularly strongly) by the steric accessibility of the group (11-14). Deviations from the VDWL are induced either by the specific interaction between the structural group and the solvent or by the nonbonding effect of a diamagnetically anisotropic solvent molecule (13, 14).

It has been demonstrated that dipole interactions induce deviations from the VDWL proportional to their intensities (13). Deviations caused by hydrogen bonds to n-electron donors, n-hydrogen bonds, are distinguished by their intensity (13). However, a relation connecting the size of those deviations with some physical property of the n-electron donor is yet to be reported. Deviations caused by hydrogen bonds to π -electron donors, π -electron bonds, are always superimposed on those resulting from the diamagnetic anisotropy of the π -orbital (20). Such deviations can be distinguished experimentally from those caused by a dispersive interaction and an anisotropic effect (14, 30). However, relations have not yet been established between the intensities of these cumulative deviations and interaction intensities.

^{13}C NMR spectra are the most useful for the study of IMI because of their good resolution and reduced possibility for peak overlaps. Besides, the interactions of the groups represented by the carbons in the ^{13}C NMR spectrum can also indicate the participation of π orbitals in IMI (15, 16). In cases where SIS can be observed for both carbons and protons, results are mutually consistent and, in some cases, they are complementary.

Experimental

PVME was obtained from Polysciences, Inc. (Warrington, Pennsylvania). Gel permeation chromatography in THF at 25°C indicates weight and number average molecular weights of $M_w = 14,000$ and $M_n = 2,000$, respectively; i.e., an M_w/M_n of 7.0 calculated as for PS. A sample of PS was used having a narrow distribution of molecular weight, with $M_w = 600$. It was obtained from Pressure Chemicals (Pittsburgh, Pennsylvania). Both polymers were atactic. Isopropyl methyl ether, IPME, was synthesized using the Williamson reaction. All other solvents were the purest commercially available grades, used without further purification.

Solutions of PS in all solvents and solutions of PVME in good solvents were prepared at 3 mol% of polymer repeat unit (3.12 g PS or 1.74 g PVME per 0.97 g mole of solvent). The solubility of PVME in n-alkanes is very low. To achieve higher concentration, saturated solutions of PVME have been prepared at $29 \pm 0.5^\circ\text{C}$.

All ^{13}C NMR spectra have been recorded at $31 \pm 0.5^\circ\text{C}$ after 10 min in situ thermostating time. The instrument used was a Varian CFT-20 Fourier Transform NMR Spectrometer (25.4 kGauss). For PVME, a minimum of 10,000 pulses had been averaged for each spectrum. Pulse width, PW , was 7 μs , and pulse delay, PD , 3s. For PS, a minimum of 5000 pulses ($PW = 19 \mu\text{s}$, $PD = 2$ s) had been averaged. Chemical shifts were determined relative to an external standard (10 vol. % p-dioxane in D_2O) and corrected for the difference in diamagnetic susceptibilities (31). Constants for refractive index (25°C) (32) and for diamagnetic susceptibility (15° to 30°C) (32) were used without further temperature correction.

RESULTS AND DISCUSSION

Rummens plots for ^{13}C NMR chemical shifts of PVME and PS in different solvents (Table I) are represented in Figs. 1 and 2, respectively. In addition, devia-

Table 1. Refractive indices (n) and Rummens Parameters (g^2) of the Solvents Used for the Rummens Plots

No.	Solvent	Symbol	n^*	g^2
1	n-hexane	C6	1.3749	0.0347
2	n-heptane	C7	1.3870	0.0363
3	n-octane	C8	1.3980	0.0378
4	n-nonane	C9	1.4045	0.0387
5	n-decane	C10	1.4113	0.0396
6	n-dodecane	C12	1.4220	0.0411
7	n-tridecane	C13	1.4253	0.0415
8	n-tetradecane	C14	1.4280	0.0419
9	n-hexadecane	C16	1.4335	0.0426
10	diethyl ether	DEE	1.3515	0.0315
11	isopropyl methyl ether	IPME	1.3576	0.0324
12	diisopropyl ether	DIPE	1.3684	0.0338
13	cyclohexane	CYCLOC6	1.4252	0.0415
14	chloroform	CHCl ₃	1.4460	0.0443
15	cumene	CUM	1.4917	0.0505
16	toluene	TOL	1.4968	0.0512
17	benzene	BENZ	1.5007	0.0517

*refractive index values at 25°C (32)

tions from the VDWL at each carbon in the molecule are represented schematically in Figs. 3 to 6. In the case of PVME only an average deviation is shown for the β carbon.

Interactions in the Blend

As can be seen in Fig. 3, IPME causes weak deshielding of unsubstituted ring carbons in PS. Both the pattern and intensities of these deviations are similar to those caused by diethyl ether and diisopropyl ether (Fig. 2). It is unlikely that ortho- and para-hydrogens from PS engage with equal intensity in interactions with the ether oxygen. The observed pattern of deviations suggests interaction through the π -orbital. Low intensities of deviations for α methyne and β methylene carbons of PS, however, suggest that these two groups do not have any specific interaction with IPME.

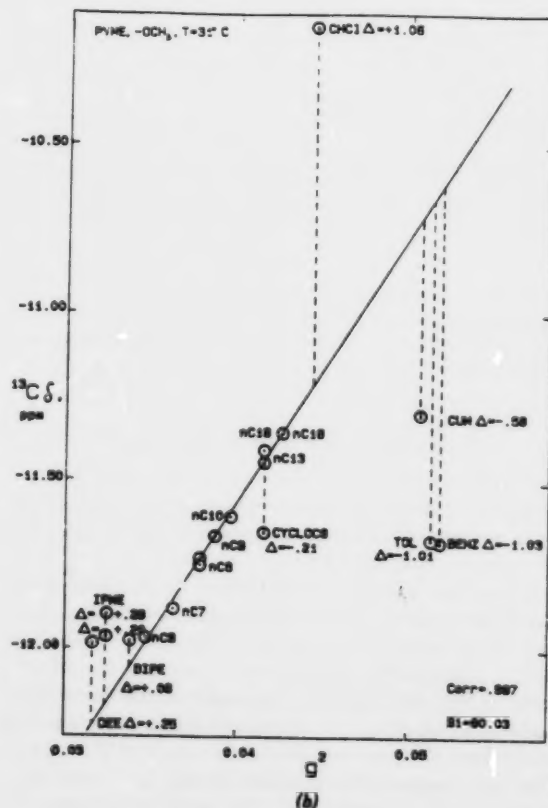
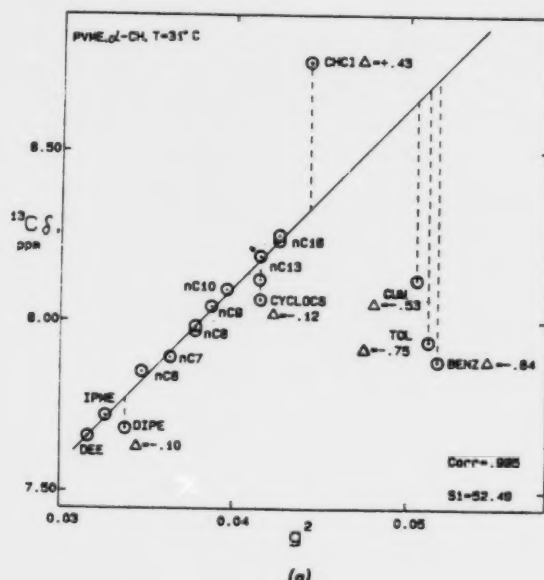
Cumene-induced deviations for PVME (Fig. 3) indicate a strong anisotropic effect of the π orbital. By analogy with previous findings (18), it may be assumed that the methoxy group is involved in the π -hydrogen bond, while other groups are involved in dispersive interactions.

Cosolution in Cyclohexane

Cyclohexane is a nonpolar compound that is believed to enter into dispersive interactions only (33). As solvent, it causes small upfield SIS, which were attributed to the ring current (34). Both PS and PVME show weak upfield deviations from the VDWL (see Fig. 4). For PVME, the relative intensities of the deviations are 3.0: 1.71: 1.0; these resemble the relative ratios of the corresponding S_1 values (2.55: 1.68: 1.0). For PS, all but the para-carbons show only negligible deviations. Those results indicate that cyclohexane behaves as a dispersive solvent for both PS and PVME.

Figure 3 shows that cyclohexane-induced deviations from the VDWL are smaller than deviations in solutions used as models for the polymer blend. It may be deduced that mutual interaction between PS and PVME is stronger than interactions of any of the two polymers with cyclohexane. This difference leads to

preferred solvation and intimate mixing. The result is formation of a compatible polymer blend when the cosolution is dried. A cosolution of the two polymers (2.5 wt. % PVME high molecular weight and 2.5 wt. % PS, 17,500) in cyclohexane forms, under different drying conditions, a transparent film.



(Caption for Figures on Page 1112 under Fig. d)

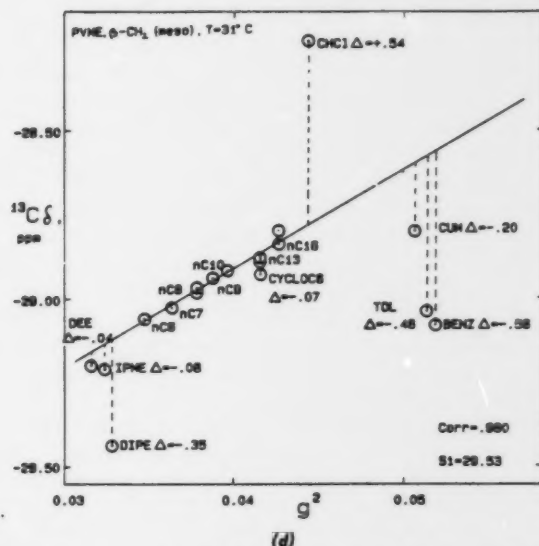
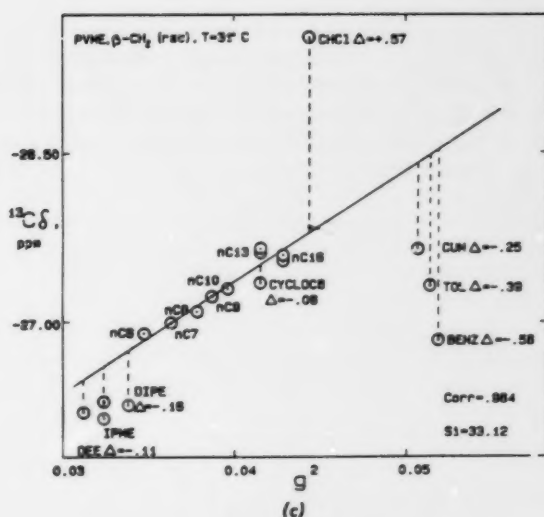


Fig. 1. Rummens plot of ^{13}C NMR chemical shifts for PVME in different solvents. Symbols as in Table 1: a) α -methylene carbon, b) methoxy carbon, c) racemic β -methylene carbon, and d) meso β -methylene carbon.

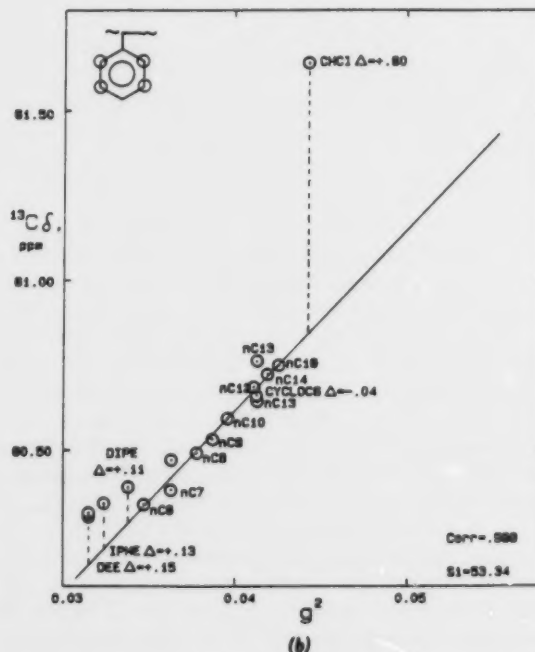
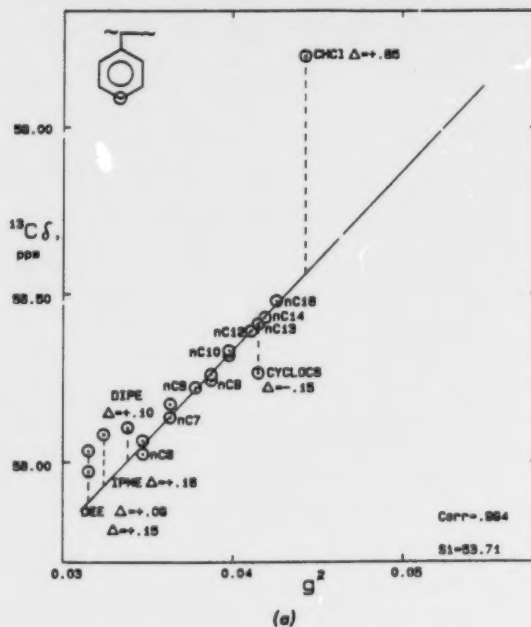
Cosolutions in Benzene and Toluene

PVME dissolved in benzene shows upfield deviations for all carbons (Fig. 5). The pattern of the deviations indicates the same character of the interaction (18) as with cumene (Fig. 3).

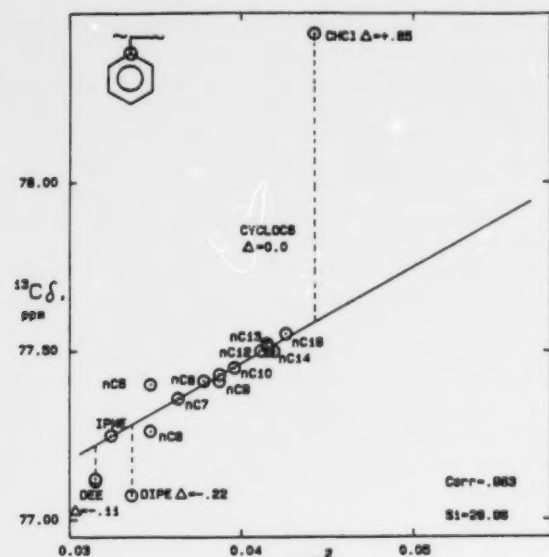
Chemical shifts for PS dissolved in benzene could not be identified. As a model for this solution, one can observe deviations for cumene dissolved in benzene (18). Upfield anisotropic deviations occur for all ring carbons (Fig. 5). It may be noticed that the substituted carbon in cumene, as well as the substituted carbon in mesitylene (18), show considerable upfield deviations. This may suggest that cumene, mesitylene, and (presumably) PS interact with benzene predominantly through parallel aromatic rings. This agrees with reported findings (35).

Deviations from the VDWL, reflecting both the interaction and the anisotropy, do not allow one to determine whether benzene interacts more strongly with PS or with PVME. It was, however, reported earlier that the solubility parameters, χ , for PS and PVME in benzene are 0.26 and 0.15, respectively (7).

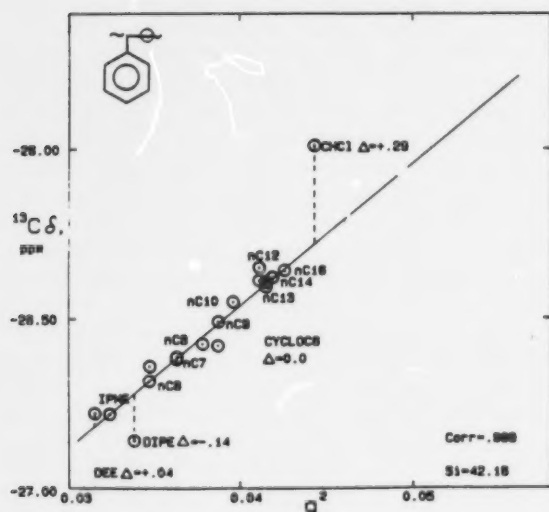
Benzene in IPME (Fig. 5) shows deshielding for carbon, which is only a little stronger than those for PS dissolved in IPME. This indicates that the characteristics of the interaction of benzene and PS with IPME (or PVME) are similar. It may also be assumed that only a



(Caption for Figures on Page 1113 under Fig. e)



(c)

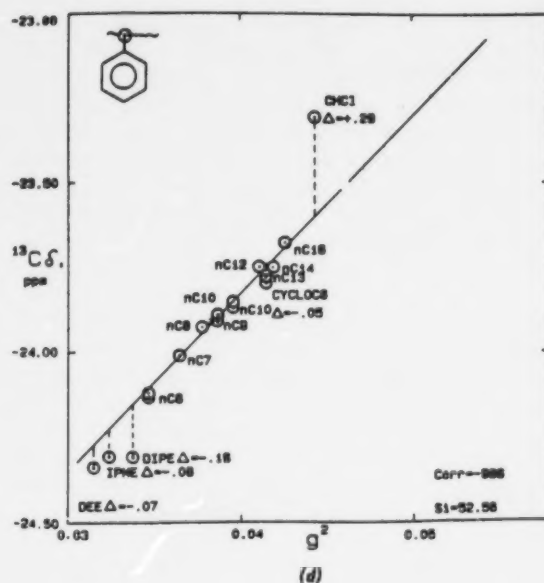


(e)

Fig. 2. Rummens plot of ¹³C NMR chemical shifts for PS in different solvents. Symbols as in Table 1: a) para carbon, b) ortho and meta carbons, c) ipso carbon, d) α carbon, and e) β carbon.

small difference exists between the energies of the interactions of the methoxy group, in PVME with benzene, and with the phenyl group in PS. This will lead to an equilibrium between the methoxy groups interacting with benzene and those interacting with the phenyl ring in PS. As the concentration of the polymers in the cosolution is increased, this equilibrium will shift more toward interaction among polymer repeat units. This would lead toward more intimate mixing between PS and PVME and, ultimately, to a compatible blend (1, 2).

PVME dissolved in toluene shows upfield deviations for all carbons with intensities similar to those induced by benzene (Fig. 1). Cosolutions of PVME and



(d)

PS in toluene yield compatible blends (1, 2). Apparently, the role of toluene is similar to that of benzene.

Cosolutions in Chloroform

PS dissolved in chloroform, CHCl₃, shows very strong deviations downfield from the VDWL for all ring carbons (Fig. 6). CHCl₃ dissolved in cumene shows deviations Δ = 0.38 ppm and Δ = 1.44 ppm in ¹³C and ¹H NMR, respectively (18). These results indicate a π-hydrogen bond between the phenyl ring in PS and CHCl₃. This agrees with published results (36, 37).

The hydrogen bond between the electron-deficient hydrogen in CHCl₃ and the ether oxygen is usually considered a predominant mode of IMI between CHCl₃ and ethers of low molecular weight (38). Results have been reported indicating the existence of more complex

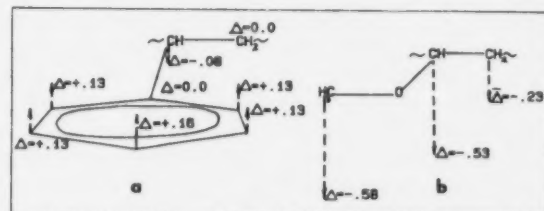


Fig. 3. Deviations from the VDWL for (a) PS in isopropyl methyl ether and (b) PVME in cumene.

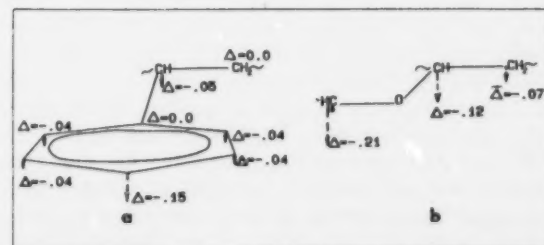


Fig. 4. Deviations from VDWL for (a) PS and (b) PVME in cyclohexane.

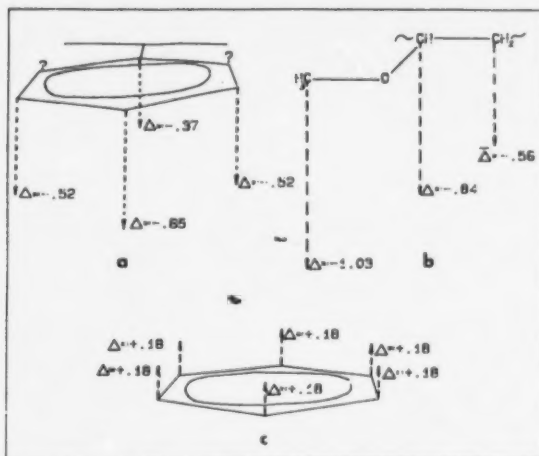


Fig. 5. Deviations from the VDWL for (a) cumene, (b) PVME in benzene, and (c) benzene in isopropyl methyl ether.

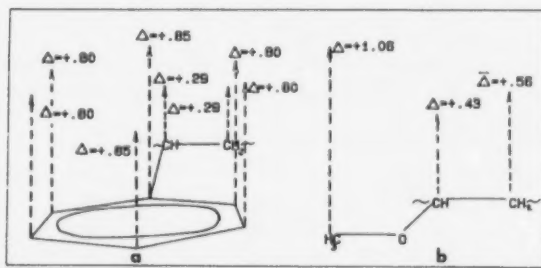


Fig. 6. Deviations from the VDWL for (a) PS and (b) PVME in chloroform.

modes of interaction between those compounds (39, 40). The second suggested mode of interaction is a charge transfer complex between chlorine and oxygen (33, 41). CHCl_3 dissolved in IPME shows deviations of $\Delta = 0.65$ ppm and $\Delta = +1.60$ ppm in ^1H and ^{13}C NMR, respectively (18). This indicates that CHCl_3 does act as a proton donor to ether but also that the $-\text{CCl}_3$ group is also significantly engaged in the interaction. PVME dissolved in CHCl_3 shows very strong downfield deviations for all carbons (Fig. 6). The large difference between the deviations for methoxy and α methylene carbons and the large deviation for the β methylene carbon indicate that interaction through the ether oxygen is not the only mode of interaction with CHCl_3 . The pattern of the deviations suggests hydrogen bonding between electron-deficient hydrogens in PVME and chlorine in CHCl_3 . The intensities of deviations (see Fig. 6) indicate that the interaction of PS with CHCl_3 is several times stronger than its interaction with IPME (Fig. 3). Considering that deviations for PVME in cumene (Fig. 3) are largely due to an anisotropic effect, one may conclude that PVME interacts much more strongly with CHCl_3 than with PS. From the ^{13}C NMR deviations for CHCl_3 induced by benzene ($\Delta = 0.38$ ppm) and by IPME ($\Delta = +1.60$ ppm), it may be independently concluded that CHCl_3 interacts more strongly with PVME than with PS. This is in agreement with the values reported for the interaction parameters

for the two polymers in CHCl_3 ($\chi = 0.13$ and $\chi = -0.92$ for PS and PVME, respectively) (7).

Apparently, strong interactions between polymers and solvent prevent the interaction between the repeat units of the two polymers in cosolution. As the concentration of the cosolution is increased, PS, which has a poorer solubility in CHCl_3 (7), separates into a new PS-rich phase. Such a two-phase solution will result in an inhomogeneous blend (1, 2).

In the cosolution of PVME and PS in CHCl_3 , the solvent affects the formation of a homogeneous blend in two ways. Firstly, it prevents the interaction among repeat units of the two polymers. In addition, different intensities of the interactions between two polymers and the solvent predetermine that they will reach critical concentrations at different cosolution concentrations. At present, it is not possible to determine the relative importance of these two solvent effects.

CONCLUSIONS

Compatibility of the cosolution-cast blends of PVME and PS depends on the competition among the intermolecular interactions between the two polymers and between polymers and the solvent.

The mutual interaction of PS and PVME is stronger than the interaction of either of the two polymers with cyclohexane. This leads to preferred solvation of the two polymers while in the solution and to intimate mixing, leading to a compatible blend. The methoxy group of PVME has similar character and only a small difference between the energies of its interaction with benzene and with PS. This leads to an equilibrium between the methoxy groups interacting with benzene and those interacting with PS. As the concentration of the cosolution increases, this equilibrium shifts toward a PVME-PS interaction, and this leads to a compatible blend.

Intensities of interactions of each polymer with CHCl_3 are considerably larger than intensities of interactions between the two polymers. In addition, CHCl_3 is a better solvent for PVME than for PS. Two polymers, being strongly solvated, cannot mutually interact while in CHCl_3 cosolution, and they do not mix. As the concentration of the cosolution is increased, the PS reaches the critical concentration first, precipitating in a separate PS-rich phase. Such an inhomogeneous solution results in the formation of an inhomogeneous blend.

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Discussion—R. S. Porter

D. D. Patterson. Roger, you mentioned the interaction between the methoxy group and chloroform as being hydrogen bonding. The chemical shift for CCl₄ is very close to the one for CHCl₃. Could you say something about the interaction between the methoxy group and the CCl₄? Do you believe that this is a dipole-induced dipole interaction or something else? This could be relevant to an interaction between, for instance, PVC and plasticizers.

R. S. Porter. I want to state this disclaimer in the beginning: as both the speaker and the editor, I wish not to purposely bias the subsequent discussion to favor the speaker. The comment by Don Patterson is excellent,

but we cannot make definite conclusions at this time. I think that your conjecture is correct; there is probably an induced dipole effect. I will quote a little experimental evidence that is quite revealing. In certain compositions involving CCl₄ and chloroform, we see two discrete shifts, two peaks, which suggest that these solvents have specific interactions that can be effectively titrated and that, beyond that concentration, they act only in a dispersive way. We actually see two discrete peaks for chlorinated solvent, but I do not believe that it is only induced dipolar effects causing the major shift. I believe that the interaction is more complex, and that further analysis will supply more information.

D. D. Patterson. Did you see something like a charge transfer interaction? I would be interested to hear what Robert Prud'homme has to say about it.

R. E. Prud'homme. I would like to add that we made some experiments where we blended different polyesters with, not only PVC where there are hydrogen bonds available, but also with poly(vinylidene chloride) and PVDC where there are CCl₂ groups available, but the α -hydrogen is not present. We did not see any difference in miscibility between one particular polyester and PVC or PVDC. It seems that the interactions of esters with the two polymers are similar or that there are two different types of interactions, both leading to bonds of similar strength.

R. S. Porter. When you say that there is a little difference, do you mean that the reason that you get systematic compatibilization with these chlorinated polymers has something to do with some induced effects rather than specific interactions? Do I read you correctly?

R. E. Prud'homme. What we have postulated so far is that we may have some sort of dipole-dipole interaction between the CCl group and carbonyl group of the polyester, but this is just an unconfirmed hypothesis. The other possibility is that hydrogen bondings may occur between the β -hydrogen and the CO groups. It is very difficult to tell, at the present time, which of these two interactions is more likely to occur.

R. S. Porter. It is interesting to know that there are, indeed, interactions with the β -hydrogens. One might have thought that they must be passive in these associations, but it seems, from chemical shifts, that they play a real role. Incidentally, I should add that we are undertaking some exciting work on polyester compatibility, with the particular aim to study polymer pairs that are miscible with and without transesterification. For a blend, we obtain a single glass transition temperature. However, for the identical composition, where the polymers were combined in two different ways (inter-chain and intrachain interactions), we obtained two different T_g . These T_g change with blend composition, giving two T_g lines.

H. P. Schreiber. Roger, the line between miscibility and the main structuring obviously is a fine one. If you take the PVME/PS pair, is there the true miscibility from the thermodynamics standpoint? What you are saying is that here, ΔG of mixing is negative. When you get an immiscible pair out of the same situation, and presumably these things then are in a metastable state,

you'll see time shifts through diffusion mechanisms back in the miscible states.

R. S. Porter. That is correct. In my view, we are working right at the edge. After all, these systems and their close relatives have both upper and lower consolute temperatures.

H. P. Schreiber. But then, for example, if you took the PVME/PS system solidified from, say, chloroform, would you see time-dependent changes in T_g shift as miscibility was reattained?

R. S. Porter. Probably, yes. A cross that we have to bear is nonequilibrium characteristics, particularly in the last stage of solvent evaporation. For example, in one of the chlorinated systems, where interactions are fairly strong, we made the films ourselves. Once formed, they were opaque; that is, phase-separated. However, they were so close to compatibility, at least when examined by the unaided eye, that just a gentlest annealing made them transparent. The differences are quite subtle.

H. P. Schreiber. We are working with poly(methyl methacrylate), not blends, but whole polymer, that is cast from solvents having different thermodynamic interactions with the polymer. It is quite dramatic to see the enormous changes in what appear to be the surface orientation of the macromolecules and, therefore, in things like retention and vapor barrier properties. These shifts characteristically vary with annealing time at temperatures above T_g , reattaining the thermodynamically stable state. I would imagine that the same thing might happen in the two component polymer systems, with presumably fairly interesting and important results on the aging effects of the pair.

R. S. Porter. I minimized the discussion on tacticity, whose effect certainly can be real. I think that, in poly(methyl methacrylate), it might become quite prominent. We know this from the characteristic ratio of syndio and isotactic dyads in PMME. The crowding is very different. This suggests that the marginal compatibilities that you are studying with solvents and that have studied at UMass with poly(ethylene oxide) might very well depend, not so much on molecular weight of the PMMA, but on the stereo placement and sequences of regularities.

L. A. Utracki. Did you study the temperature effects? What is happening with all these shifts when the temperature approaches the immiscibility, the upper or lower critical solubility temperature?

R. S. Porter. We did not study the temperature effects, but we have some information. Unfortunately, we did not look at the subtleties, which could be interesting. For example, in the case of PVME, the insolubility above lower consolute temperature was the disconcertion of the student who put the solution in the NMR. By not being able to look inside, he did not realize that phase separation had occurred. Suddenly, the sample had disappeared, so to speak. There were no sharp line spectra. In other words, we know that phase separation would produce the changes in chemical shifts, but we did not yet look at the subtleties of the phase separation in order to see shifts at that point. There must be some information just before the lines disappear due to lack of motion and instability. There should be some interesting data to measure as we approach the border. That could be very useful.

Compatibilization of the Polystyrene/Poly(Ethyl Acrylate) and Polystyrene/Polyisoprene Systems through Ionic Interactions*

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Interactions between anions on one polymer chain with cations on another can lead to compatibilization of otherwise incompatible materials. Thus, if 5 mol% of $\sim\text{SO}_3\text{H}$ groups are attached to polystyrene, and 5 mol% of vinyl pyridine is copolymerized with ethyl acrylate, proton transfer occurs upon mixing, and the pairwise attractive interactions between the resultant ions compatibilize the blend. The same has been observed for the styrene-vinyl pyridine and sulfonated polyisoprene polymer pair. Dynamic mechanical and optical properties are used as a measure of compatibilization.

INTRODUCTION

In recent years, polymer blends have been the subject of a large number of investigations (1-3), of which many have been devoted to the problem of compatibility. Most polymer pairs are not compatible because, in contrast to low-molecular-weight materials, the entropy of mixing of two macromolecules containing a large number of segments is relatively small, while the enthalpy of mixing is usually positive or near zero, unless specific interactions are present.

Since compatible blends sometimes present advantages over incompatible blends, many attempts have been made to enhance the compatibility of polymers. These have included copolymerization of the first monomer with a small amount of the second, as well as the introduction into the system of covalent crosslinks (4) or of interacting groups leading to the formation of H-bonds (5), charge-transfer complexes (6), interpenetrating networks (7), or dipole-dipole interactions, as is widely believed to be the basis for compatibility in most PVC blends. Lastly, mention is made of the work of Longworth (8), who reports increased compatibility of 1-olefins by grafting a carboxylic acid unit onto one polymer and a basic species onto another. Following mixing of both polymers, a more compatible blend results, possibly due to hydrogen-bond interactions.

One system that is quite relevant to the present work is the formation of polyelectrolyte complexes. Michaels and Miekka (9) found that a mixture of aqueous solutions of sodium polystyrene sulfonate and poly(vinylbenzyltrimethylammonium chloride) resulted in a precipitate in which stoichiometric quantities of the ionic moieties were present. The washed product was

claimed to be practically free of microions (Na^+ or Cl^-). These materials do not dissolve in pure solvents, but do absorb great amounts of water. In the dry state, they are hard, brittle, and have a very high glass transition temperature; consequently, most of their applications are in a water-swollen state, where they exhibit properties typical of hydrogels.

PRESENT WORK

This communication deals with a procedure that can be used to compatibilize a very wide range of two either incompatible or slightly compatible polymers or polymer/plasticizer systems. Briefly, the method involves incorporating small amounts of specifically interacting acidic and nonionic basic groups onto the two materials to be compatibilized. Specifically, a report is given here of the results obtained by incorporating small amounts of styrene sulfonic acid (SSA) onto a polystyrene (PS) chain and a similar quantity of 4-vinyl pyridine (4VP) onto a poly(ethyl acrylate) (PEA) chain to compatibilize the otherwise incompatible PS/PEA system. Similarly, the sulfonation of polyisoprene (PIP) and its subsequent addition to a copolymer of styrene and 4VP results in a compatible blend, whereas esterification of the sulfonic acid groups renders the system incompatible. The success of this method depends on the transfer of the proton from the acid to the base, resulting in the formation of an ion pair, in the complete absence of microions. The general scheme is illustrated in Fig. 1.

EXPERIMENTAL

Materials

PS was obtained from Polysciences (M.W. = 125 to 250K) and sulfonated using the procedure developed by Makowski, *et al.* (10). PIP (*cis* PIP Natsyn 2200) was

*This article is a review of work recently reported in the *Journal of Polymer Science*.
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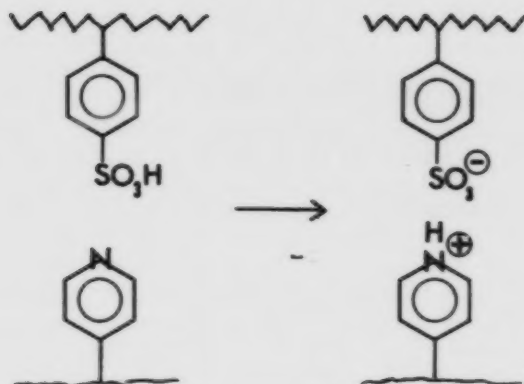


Fig. 1. General scheme for the interaction of pendant sulfonic acid and pyridine groups on polymer chains.*

kindly furnished by Dr. K. W. Scott and Mr. D. W. Stiff of the Goodyear Tire and Rubber Company. The sulfonation procedure used to obtain sulfonated PIP (S-PIP) has been described elsewhere (11). The material is partly cyclized. Esterification of the S-PIP was performed as described in Ref. 11.

PEA-co-4VP and PS-co-4VP, kindly supplied by Mr. Denis Duchesne and Miss Sylvie Gauthier, were prepared by random radical copolymerization at low conversion using benzoyl peroxide as initiator (12, 13).

Blending

PS-co-SSA and PEA-co-4VP were separately dissolved in tetrahydrofuran in stoichiometric amounts of interacting acidic and basic groups to yield dilute (1 to 3%) solutions. Similarly, S-PIP and PS-co-4VP were dissolved in a benzene-methanol (90/10:v/v) mixture. The PEA-co-4VP solution was added dropwise to the vigorously stirred PS-co-SSA solution, yielding a gel-like precipitate that was then filtered and dried in vacuo for 18 h at 70°C. In an analogous fashion, the S-PIP solution was added to the PS-co-4VP solution, resulting in gelation when the comonomeric interacting group content was 5% or more; the mixture was then stirred for one hour and subsequently freeze-dried. The blend of the PS and PEA homopolymers was prepared in the same fashion as the PS/PEA blends, with the exception that the mixture resulting from the addition was precipitated in cyclohexanol.

The blends and their precursors are described in Table 1. The blends are designated by the major constituents of their precursors, followed by the nearest integer of the average functionality content (in mole%) of their precursors.

PS-co-methacrylic acid and PEA-co-acrylic acid were separately dissolved in a benzene/methanol (90/10:v/v) mixture in stoichiometric amounts of ionic groups. Following neutralization with methanolic NaOH, the solutions were mixed and the resulting mixture freeze-dried.

Dynamic Mechanical Studies

Dynamic mechanical (DM) studies were performed on a torsional pendulum operating from -100° to 200°C at frequencies between 4 and 0.1 Hz, at a heating rate of approximately 0.5 to 1.0 deg./min. Samples used in these measurements were made by compression molding 0.8 g of the blend at 50° to 130°C (depending on the sample) for about one hour at 9,000 to 16,000 PSI. Typical sample dimensions were 2.5 · 5.5 · 50 mm.

RESULTS

PS/PEA System

Figures 2 and 3 show the storage modulus and the loss tangent as a function of temperature for Blends PS/PEA-0 and PS/PEA-2, respectively. The two-step descent of G' , accompanied by the two loss tangent maxima at ca. -10° and 100°C, correspond to the glass transitions of PEA (or PEA-co-4VP) and of PS (or PS-co-SSA). The presence of these two separate transitions in the blends, coupled with their opacity (caused by the difference in the refractive indices of the finely dispersed phases), are a clear indication of the incompatibility.

Figure 4 shows the DM properties of Blend PS/PEA-5 and clearly indicates that compatibility is achieved, as evidenced by the single, albeit broad, loss tangent maximum accompanied by the single-step descent in G' at ca. 72°C. The sample is also transparent. Blend PS/PEA-10 exhibits properties that are quite similar to those of Blend PS/PEA-5, except for a shift in the glass transition temperature to ca. 90°C.

It was of interest to ascertain, at this point, whether coulombic interactions of whatever type by themselves were sufficient to achieve compatibilization. Therefore, the DM properties of a blend of sodium PS-co-methacrylic acid (comonomer content 6.4 percent) and sodium PEA-co-acrylic acid (comonomer content 6.4 percent) were measured and are presented in Figure 5. Incompatibility is again demonstrated by these results as well as by the opacity of the sample. To verify that the presence of groups capable of H-bonding is not sufficient to compatibilize this system, a blend was prepared of PS-co-methacrylic acid (comonomer content 5.7 percent) and PEA-co-4VP (comonomer content 6.4 percent). The blend was opaque and, hence, incompatible.

PS-PIP SYSTEM

Figure 6 shows the DM properties of Blend PS/PIP-0; clearly, the blend is incompatible with glass transitions at -61°C (PIP) and 100°C (PS). In Fig. 7, the DM properties of Blend PS/PIP-2 are presented, with two loss tangent peaks occurring at 0° and 114°C; again, both Blends PS/PIP-0 and PS/PIP-2 are opaque.

Figure 8 shows the results obtained for Blend PS/PIP-5; at this point, the two glass transitions have coalesced into a single, broad transition, and compatibility is confirmed from the transparency of the samples. Blends PS/PIP-7 and PS/PIP-10 exhibit properties quite similar to those of Blend PS/PIP-5, with a slight upward shift in the glass transition temperature.

* Reproduced from P. Smith and A. Eisenberg, *J. Polym. Sci.*, in press.

Table 1. Composition and Glass-Transition Temperatures of the Salts of the Precursors and of the Blends

Blend	Mole% sulfonation in S-PIP	T _g ^a of Na salt of S-PIP ^{**}	Mole% 4VP in PS copolymer	T _g ^a of quaternized ^{***} PS copolymer	Temperature of tan δ maximum in blend
PS/PIP-0	0	-61°C	0	100°C	-61°C, 100°C
PS/PIP-2	1.83	0°C	2.10	115°C	0°C, 114°C
PS/PIP-5	5.25	65°C	5.06	130°C	85°C
PS/PIP-7	7.43	125°C	7.61	135°C	121°C
PS/PIP-10	9.31	—	10.01	145°C	142°C

Blend	Mole% sulfonation in PS copolymer	T _g ^a of Na salt of PS copolymer	Mole% 4VP in PEA copolymer	T _g ^a of quaternized ^{***} PEA copolymer	Temperature of tan δ maximum in blend
PS/PEA-0	0	101°C	0	-13°C	-7, 106°C
PS/PEA-2	1.75	115°C	1.65	—	-3, 89°C
PS/PEA-5	5.1	124°C	5.4	4°C	72°C
PS/PEA-10	9.9	139°C	10.5	19°C	90°C

^a From tan δ measurements at 1 Hz.

^{**} The T_g's of the sulfonated isoprene salts are much higher than expected. It has been established that this is due to cyclization of the polyisoprene units during the sulfonation reaction (11).

^{***} Quaternized with CH₃Br.

To demonstrate that the specific ionic features make them compatible, an esterified sample of the S-PIP containing 5 mol% sulfonate groups was mixed with PS-co-4VP (4 VP content 5 percent). The DM study results (Fig. 9) show a reestablishment of the two loss tangent maxima at the glass transition temperatures of the salts of the precursor; the sample is now opaque. Hence, incompatibility results from the removal of the specific interaction. Finally, in Table 1, a list is given of the glass transition temperatures of the salts of the precursors and the Blends.

DISCUSSION

Compatibility occurs in both PS/PEA and PS/PIP (partly cyclized) systems when the interacting group content is 5 percent or higher. In both systems, the glass transition temperature of the blend usually falls close to halfway between those of the salts of the precursors. Below the threshold group content, which is probably a function of the strength of the interaction, samples are opaque and possess two loss tangent maxima at approximately the same temperatures as the glass transition temperatures of the salts of the precursors. However,

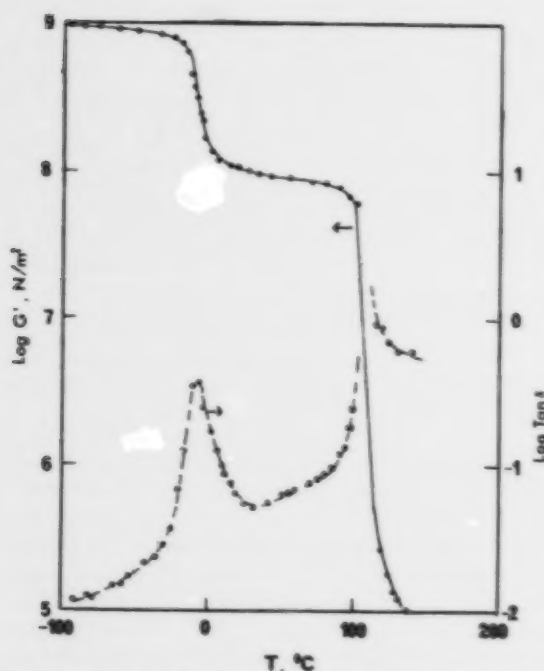


Fig. 2. Variation of the shear storage modulus (G') and the loss tangent ($\tan \delta$) with temperature for a 50/50 blend of PS and PEA.*

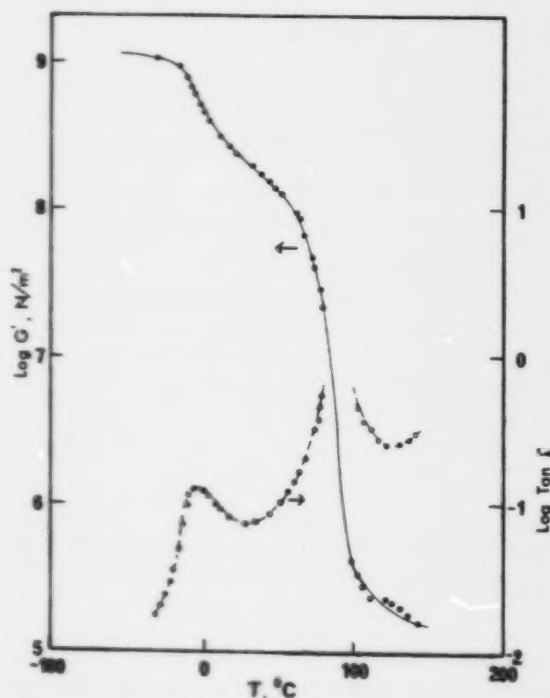


Fig. 3. Variation of the shear storage modulus (G') and the loss tangent ($\tan \delta$) with temperature for Blend PS/PEA-2.*

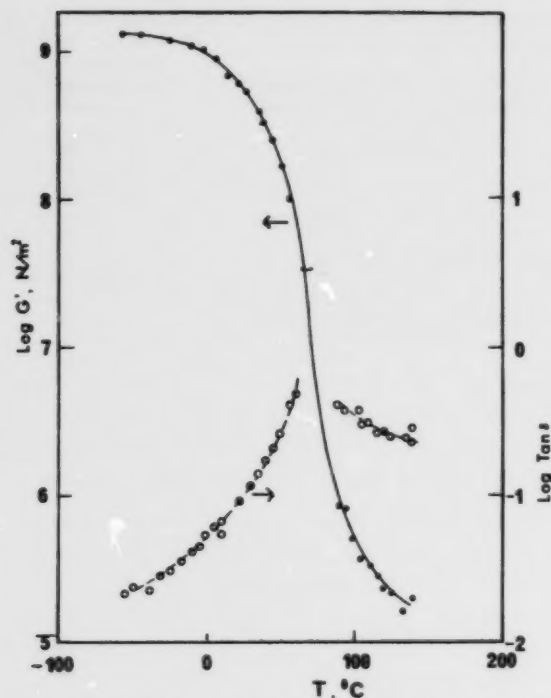


Fig. 4. Variation of the shear storage modulus (G') and the loss tangent ($\tan \delta$) with temperature for Blend PS/PEA-5.*

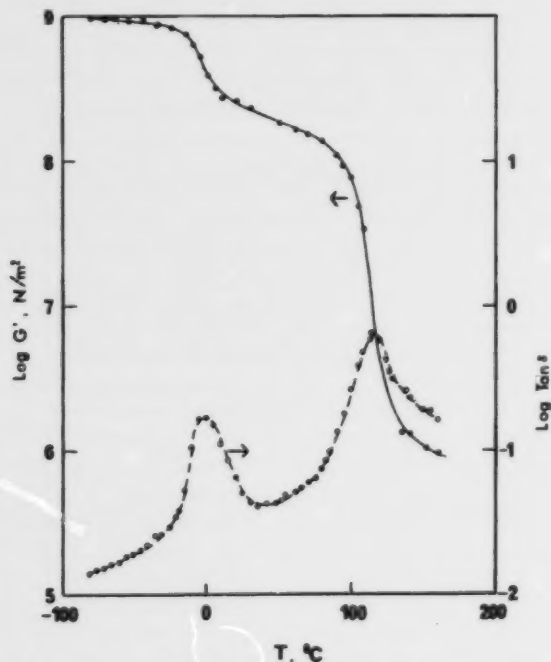


Fig. 5. Variation of the shear storage modulus (G') and the loss tangent ($\tan \delta$) with temperature for a blend of the sodium salts of poly(styrene-co methacrylic acid) and poly(ethyl acrylate-co acrylic acid).*

even below this threshold, compatibility appears to have increased with respect to the blends of the unmodified homopolymers, as the broadening of the transitions in DM properties seem to indicate.

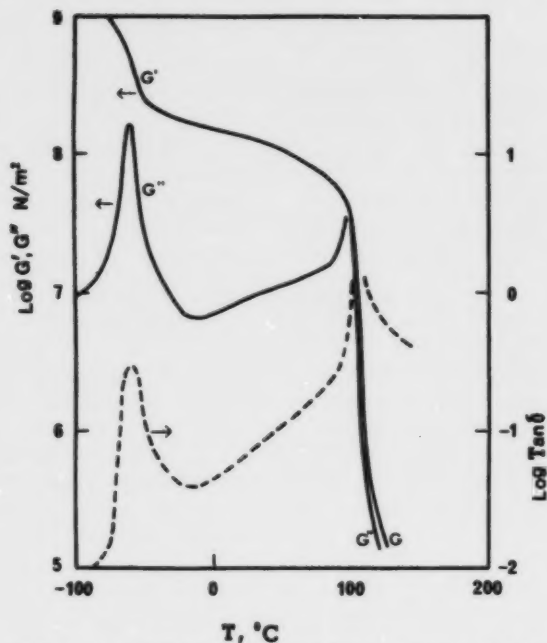


Fig. 6. Variation of the shear storage modulus (G'), the shear loss modulus (G''), and the loss tangent ($\tan \delta$) with temperature for a 50/50 blend of PIP and PS.**

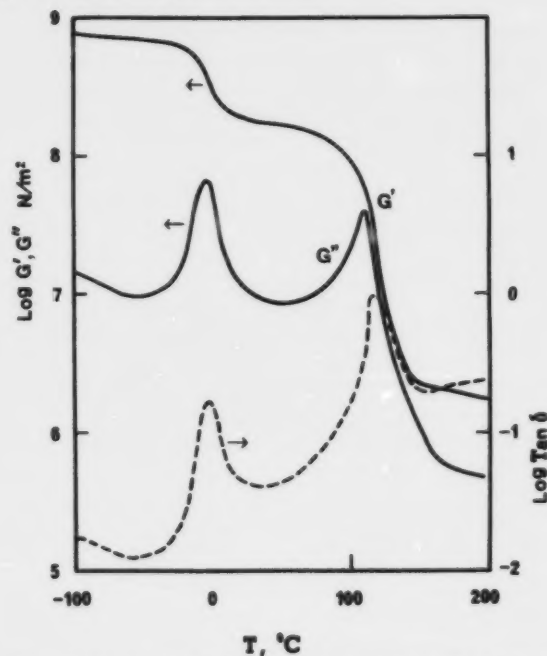


Fig. 7. Variation of the shear storage modulus (G'), the shear loss modulus (G''), and the loss tangent ($\tan \delta$) with temperature for Blend PS/PIP-2.**

In the PS/PEA system, protonation of the pyridine ring, confirmed by infrared spectroscopy (14), yields ion pairs that, through coulombic interactions, compatibilize the otherwise incompatible system. The presence of ionic interactions alone between similar pendant groups (i.e., sodium carboxylate) on the two

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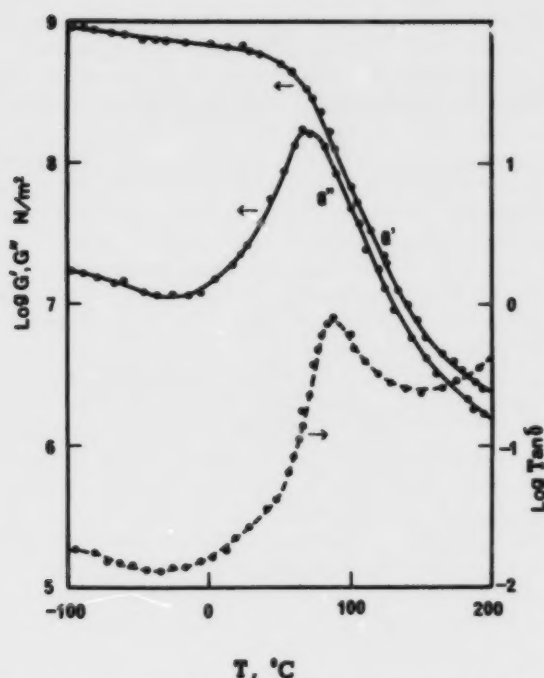


Fig. 8. Variation of the shear storage modulus (G'), the shear loss modulus (G''), and the loss tangent ($\tan \delta$) with temperature for Blend PS/PIP-5.**

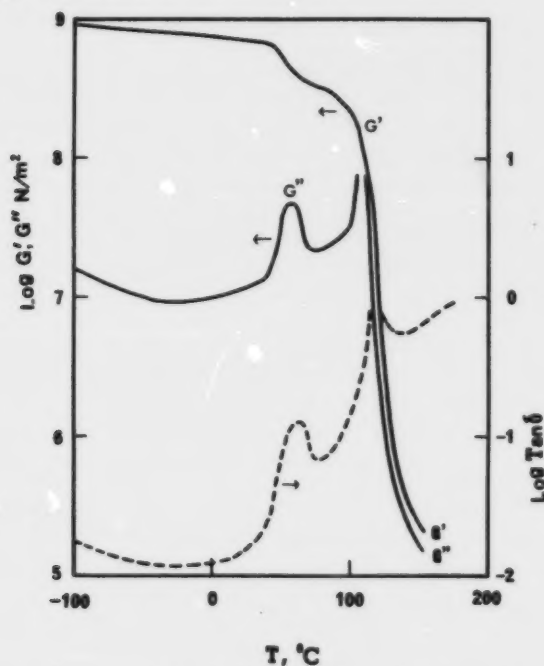


Fig. 9. Variation of the shear storage modulus (G'), the shear loss modulus (G''), and the loss tangent ($\tan \delta$) with temperature for a blend of esterified S-PIP (5.25 mol% sulfonation) and PS-co-4VP (4VP content 5.06%).**

polymers in the PS/PEA system does not constitute a sufficiently strong driving force to accomplish mixing, as evidenced by the incompatible blend of the sodium salts of PS-co-methacrylic acid and PEA-co acrylic acid. Similarly, the presence of pendant groups capable of

hydrogen-bonding does not compatibilize this system, as evidenced by the opacity of the PS-co-methacrylic acid and PEA-co-4VP blend.

NOMENCLATURE

PS	= Polystyrene
SSA	= Styrene Sulfonic Acid
4VP	= 4-Vinyl Pyridine
PEA	= Poly(Ethyl Acrylate)
PIP	= Polyisoprene
S-PIP	= Sulfonated Polyisoprene
DM	= Dynamic Mechanical

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Discussion—A. Eisenberg

K. C. Frisch. I would like to compliment Professor Eisenberg for an excellent and interesting work. It certainly opens up many new avenues. Over the last couple of years, we have used some of the principles in preparing the polyelectrolytes or networks to get compatibility, not only with linear polymers. We can apply this principle to the situation in which one of the polymers would be crosslinked and the other linear or vice-versa, as well as where both are crosslinked, as is the case for IPNs, which I'm going to present today. Exactly the same principle that you have just enumerated can be very nicely applied to systems that otherwise one could not even think to compatibilize. Your approach is indeed workable in a broad way.

A. Eisenberg. In other words, you have anionic and cationic interpenetrating polymer networks?

K. C. Frisch. Exactly.

R. S. Porter. Adi, three small comments regarding the morphology and rheology: first, could it be that certain of the ion-containing materials are lamellar and certain are clustered? You mentioned one or the other. It seems to me that we could consider them as a class of inverted micelles; some would be thread-like and some would be cluster-like. Similarly, soap and oil form thread-like, rather than cluster-like, structures. Then

there is the rheology that goes with this. We talk about enormous viscosities. These systems may flow by yield, as they might actually have an indefinitely high viscosity. It would take the shifting of one ion from one cluster to another to actually facilitate total molecular translation. In this manner, the flow would be by yield rather than by normal Newtonian behavior. Then, the final point: I would expect that $\tan\delta$, which you utilized, would be amplitude dependent. The amplitude corresponds to displacement distance between domains. It would be crucial whether the domains are disrupted during the oscillation period or not. I wonder if you have examined that.

A. Eisenberg. We have looked at amplitude dependence in both ionic and nonionic systems and find that there is an amplitude dependence. However, we have ascribed it to instrumental difficulties, rather than real material properties, because we have seen it in both ionic and nonionic systems. These are not very big effects, 2 to 3 percent. The amplitude decays a little bit faster at very high amplitudes. We have not been able to relate this to materials. Furthermore, we have not really used large amplitude oscillations, nothing like 30° or 40°, we used 2° or 3°. In the limit of 1° to 2°, there does not seem to be any dependence.

R. S. Porter. I would expect that, at a large amplitude, one would set in a time-averaged orientation in the direction of the strain imposed as an indicator of the disruption of domains.

A. Eisenberg. We have not looked at that at all.

L. A. Utracki. This must also be frequency-dependent, as well.

A. Eisenberg. Yes, it is.

L. A. Utracki. I have a couple of comments and questions. First of all, I would like to thank Dr. Porter for commenting on the mechanisms of viscosity. I recently published an article treating this issue for ionomers. Changing the temperature, one observed different mechanisms of flow. I proposed to consider this as due to the destruction of clusters. You will find support for your ideas in the other works on the mechanisms of viscous flow. Adi, I am surprised that you do not see this type of transition in anionic systems, the type you observed in cationic. How do you explain this? Apparently you are not getting any more of the same crosslinks by cluster mechanisms.

A. Eisenberg. The simplest explanation that comes to mind is based on the very large size of both the cations and anions. The distance between the centers of charge, instead of 1½ to 2Å (in the carboxylates), is 4 to 5Å for the chloride, bromide, or iodide anions and pyridinium cations. In addition, there is a certain polarization of the benzene ring. The sizes of the ions are, therefore, large. Because of the large size of the ions, you pay a very much smaller penalty for pulling ion pairs or ion quartets apart or, inversely, you get very much less back when you put these ions together. There is probably not

enough driving force to give you large clusters, and you get only small multiplets. Because of the large size of the anions and the cations, those multiplets tend to fall apart at the T_g . I should add that Otocka and Eirich, a number of years ago, looked at rubbers containing pyridinium cations and carboxylate anions. They found that, in materials with very low T_g s there was a very definite cross-linking resulting from the ion interactions, which we do not see in the high- T_g materials.

L. A. Utracki. The other question: Roger commented on the effect of annealing. Did you see an effect of annealing on your samples? Are your samples prepared from solution?

A. Eisenberg. No, we are freeze-drying them and compression molding the freeze-dried products.

L. A. Utracki. Did you check for effects of annealing?

A. Eisenberg. There are annealing effects in regular ionomers. For instance, if you take styrene/sodium methacrylate copolymers and heat them up the first time, you get a normal expansion in the glassy state but a very low expansion coefficient above the glass transition temperature. Then, when you cycle above the glass transition temperature, you get a high, normal, liquid-like expansion coefficient. So, yes, there are annealing effects on ionomers that are unblended. I suspect that we would also find them in the blended ionomers, but we have not looked for them.

L. A. Utracki. I referred, rather, to the poly(vinyl pyridine) type. Did you see any shift in the viscoelastic spectrum with the annealing or not?

A. Eisenberg. We have not looked for it. This certainly will be something interesting to do.

L. E. St-Pierre. When you are talking about the size of the ion clusters or the ions, you are harking back to your previous work, where you looked at the effects of hydration and humidity. The ease of dissociation is going to be affected by that. Of course, the ion size will depend upon hydration. Have you begun to look at that in his last work?

A. Eisenberg. Not at all.

V. Di Tullio. If the anion size is so important, then what about the cation size when you consider the phosphates; for example, calcium vs. magnesium.

A. Eisenberg. Sure, the cation size is very important. That is what gives us the large variation of the glass transition temperature.

V. Di Tullio. I do not remember your first slide, but was that a really dramatic difference?

A. Eisenberg. For nonionic phosphates, the T_g is -10°C. I don't have the results for potassium here, but the T_g is about 220°C, and for the calcium phosphates, 520°C; cesium would be 180°C or so.

V. Di Tullio. You are talking about divalent vs. monovalent cations. Let us take mono vs. mono or di- vs. di-

A. Eisenberg. All right. Take lithium phosphate, with a T_g of 330° and the cesium salt, which we extrapolated to about 180°; you have a 150° difference.

Siloxane-Poly(methylmethacrylate) Amphoteric Blends

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Poly([4-(methacryloyloxy) butyl]pentamethyldisiloxane), PMBPD, has been prepared for the first time. At the weight average molecular weight of 55,900, it is a clear, viscous liquid with a glass transition temperature, T_g , of 236K. Copolymers with methylmethacrylate have also been prepared. The homo- and copolymers, all of which have methacrylate backbones with pendant siloxane groups, were blended with poly(methylmethacrylate), PMMA. Using the existence of a single T_g as a definition of miscibility, it was found that blends of either PMMA or PMBPD with random copolymers are miscible. However, in spite of a clear appearance, the blend of the two homopolymers were found to have two distinct T_g s.

INTRODUCTION

The conventional technological goals for the blending of polymers have seen improvement or at least retention of the mechanical and processing properties that lead to improvement of economics. Poly(2,6-dimethyl-1,4-phenyleneoxide)-styrene blends are an example for which enhancement is realized in all three categories. Recent developments in ophthalmological applications suggest that other physical properties can also be of importance in measuring the value of a blend (1).

Historically, two major developments in contact lenses are identifiable. The contact lenses first used were "hard" poly(methylmethacrylate) (PMMA) lenses. Later, a "soft" lens, consisting of PMMA having a hydrophilic component, largely replaced the use of the "hard" lens. The "soft" lens has a biocompatible surface and also affords enhanced oxygen transport to the surface of the eye via the swollen hydrophil on the inner surface of the lens.

During the past four years, a new "hard" lens has been developed that allows oxygen permeation through the lens to the surface of the eye. The material from which this lens is formed is a copolymer of methylmethacrylate (MMA) and a siloxane-containing methacrylate, such as 1,3-(4-methacryloyloxybutyl)tetramethyldisiloxane (2). Copolymers having up to 10 percent siloxane by weight have been prepared. Typical 20-fold enhancement of oxygen transport, over that of pure PMMA, has been observed (3). Furthermore, the excellent optical clarity of PMMA has been retained. Obviously, the copolymer structure does not allow aggregation of the siloxane moieties to proceed to the

point where light scattering is significant. There is no specific interaction in evidence for these two polymers. Hence, the use of the two-component solubility parameter approach ($\delta_{PDMS} = 7.5$, $\delta_{PMMA} = 11.0$ (4)) suggests that miscibility is unlikely (5).

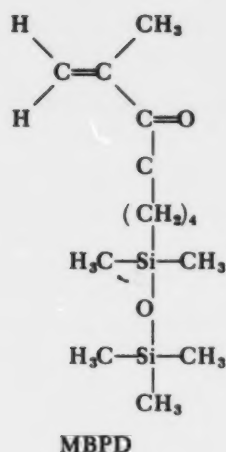
An investigation of the properties of silicone-acrylate copolymers is underway in our laboratory. Recently, the blending of these with PMMA and PDMS has been attempted. This communication describes the results to date, involving the synthesis of the siloxymethacrylate monomer, its polymerization and copolymerization with MMA, and the study of the properties of several blends.

Solution properties and further blending experiments will be reported in the near future.

EXPERIMENTAL

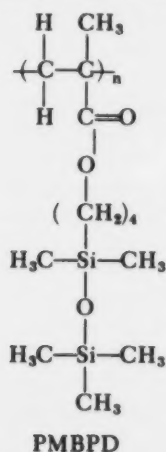
Synthesis of [4-(methacryloyloxy) butyl]pentamethyldisiloxane, MBPD (6)

A mixture of 65.1 g of 1,1-dimethyl-1-sila-2-oxacyclohexane, 42.6 hexamethyldisiloxane (Petrarch Systems Inc.), 44.1 g methacrylic acid (Aldrich Chemical Co.), and 3.5 g H_2SO_4 was refluxed with stirring in the presence of 1,000 ppm hydroquinone for 3.5 h at 95°C. When the reaction mixture was cooled, it separated into two layers. The lower layer was discarded, while the upper layer was washed twice with 5 percent aqueous sodium carbonate, followed by centrifugation for 30 minutes. The resulting brown-colored liquid was dried with sodium sulfate. Vacuum distillation yielded 40.8 g of product with a boiling range of 89° to 92°C at ~2 torr. The NMR of the product confirmed it to be MBPD. The product was stored under nitrogen at 5°C.



Polymerization of MBPD (7)

A 100 ml glass cylinder with a Teflon stopcock was charged with 29.7 g of MBPD, 0.054 g of 2,2'-azobis-(2-methyl-propionitrile) (AIBN) and 20.1 g of dimethyl-formamide (BDH Analytical Reagent, distilled under nitrogen) (DMF), evacuated and placed in an oil bath at 95°C and allowed to polymerize for 35 min. The contents were then cooled and dissolved in 200 ml of toluene. The polymer was precipitated by rapidly pouring the toluene solution into 1,500 ml of ice-cold methanol. The supernatant was decanted off, and the remaining solvent was removed from the polymer in a vacuum oven at 60°C. The NMR spectrum of this polymer (PMBPD) was consistent with the structure:



Preparation of PMMA and of Copolymers of MMA and MBPD

PMMA and two copolymers with nominal weight ratios of MMA:MBPD of 2:1 and 4:1 were synthesized. The procedure used for the polymerizations was identical to that for the polymerization of MBPD (see last section). The quantities of chemicals and polymerization procedures are shown in Table 1. For additional purification, the copolymers were reprecipitated by the addition of a solution of the copolymer in 3:1 benzene:chloroform to cold petroleum ether (boiling range 30° to 60°C). The supernatant was decanted off, and the

remaining solvent was removed from the polymers in a vacuum oven, yielding white powders.

Preparation of Blends

Blend A was prepared by dissolving 2.054 g of PMMA and 0.371 g of PMBPD in methylene chloride. Thin films were formed by pouring the solution into a Petri dish and evaporating the solvent, first in air and then in a vacuum oven, for 24 h at 130°C.

Blend B was prepared by dissolving 0.5325 g of copolymer 1 and 0.0418 g of PMBPD in THF and by evaporating the solvent slowly under air and then in a vacuum oven at 60°C for 2 days.

Blend C was prepared by dissolving 0.74 g of copolymer 2 with 0.74 g of PMMA in 50 ml THF. The solvent was removed under vacuum for 3 days at 30°C.

Blend D was prepared in an identical manner to Blend C but had a composition of 0.5 g copolymer 1 plus 0.56 g of PMMA.

Thermal Analysis

Differential scanning calorimetry was performed on a Perkin-Elmer DSC-2 on the samples to determine glass-transition temperatures.

Molecular Weight Determination

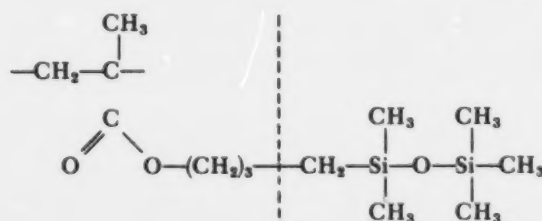
The molecular weights of the polymers ($\bar{M}_n$, $\bar{M}_w$) were determined by "Waters Associates" on a gel permeation chromatograph, (Model 244 with Data Module, model 730, with GPC option).

Copolymer Composition Determination

The compositional analysis of the copolymers were made by high-resolution NMR and was based on the comparison of the peak heights of the methacrylate methyl and the silyl methyl.

RESULTS AND DISCUSSION

The compositions and properties of the homo- and copolymers are listed in Table 2. The calculation of the weight ratios, acrylate to siloxane (column 3), is based on the scission of PMBPD at the methylene group adjacent to the silicon atom; thus:



Fragment weight = 127

Fragment weight = 161

PMBPD is a clear, highly viscous liquid. The two copolymers were clear, rigid glasses having the general appearance of PMMA. The compositions and properties of the four blends are shown in Table 3.

The results, despite their preliminary nature, are most interesting and suggest that the final net composition of the blend is less important in determining the

Siloxane-Poly(methylmethacrylate) Amphoteric Blends

Table 1. Conditions for the Polymerization of MMA and the Copolymerization of MMA and MBPD

Designation	MMA: MBPD (weight ratio reactants)	Polymerization Solution MMA (g)	MBPD (g)	AIBN (g)	DMF (ml)	Temp. (°C)	Time (min)
Copoly 1	2:1	11.0	5.65	0.064	22	95	35
Copoly 2	4:1	19.92	5.42	0.130	22	95	35
PMMA		23.14	0	0.120	49	100	50
PMBPD	0:1	0	29.7	0.054	22	95	35

Table 2. Polymer Compositions and Properties

Polymer Molar Composition	Designation	Weight Ratio Acrylate/Siloxane	T_g (K)	$\bar{M}_n$	$\bar{M}_w$
PMMA	PMMA		394	22,600	53,700
PMBPD	PMBPD	0.8:1	236	55,900	133,200
MMA _{4.5} (MBPD)	Copolymer 1	3.8:1	356	29,800	78,000
MMA _{10.2} (MBPD)	Copolymer 2	7.1:1	370	27,400	63,800

Table 3. Blend Compositions and Properties

Blend	Weight Ratio Acrylate/Siloxane	Feed	T_g (K)	Appearance	Surface
A	10/1	PMMA + PMBPD	236 and 394	Clear	Sticky
B	10/3	Copoly 1 + PMBPD	345	Clear	Sticky
C	10/0.7	PMMA + Copoly 2	388	Clear	Hard
D	10/1	PMMA + Copoly 1	broad 356	Clear	Hard

miscibility of two polymers than is the nature of the species contributing to that composition.

The single T_g , which (by the operational definition) indicates homogeneity in Blends C and D, is not surprising, since the siloxane content in both blends is achieved via a copolymer rich in methacrylate monomer. However, Blend A represents a sharp contrast to Blends C and D in that, with the same net composition, there is no evidence of homogeneity. In this case, while the polymer backbone is entirely methacrylate, the proximity on each segment of a sizeable siloxane entity apparently precludes the solution of PMBPD in PMMA. Blend B, for which the ratio of siloxane to acrylate is three times that contained in the other blends, exhibits but one T_g , indicating that it is largely homogeneous. A qualification to this conclusion must be made, in that the surface of Blend B had a slight stickiness, which suggests that not all of the PMBPD was contained in the interior of the sample.

The T_g of Blend B was calculated on the basis of the work of Mandelkern, *et al.* (8):

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (1)$$

where T_{g1} and T_{g2} are the glass transition temperatures for copolymer 1 and PMBPD and w_1 and w_2 , their weight fractions. Solution of this equation predicts a value of 342K for the blend T_g . This is remarkably close to the experimental value of 345K.

In summation, the results indicate that an "amphoteric" homopolymer of the PMBPD type, where the

backbone is identical with the structure of a homopolymer and in which the side chains have the nature of a second homopolymer, can affect the cosolubility of polymers of greatly differing solubilities. However, thus far, it seems that this effect is limited to blends with copolymers. A generalized structure of this class of polymers is shown in Fig. 1.

Further studies, aimed at reinforcing and extending the present work, are underway.

ACKNOWLEDGMENTS

The financial support of the Natural Science and Engineering Research Council and the Quebec Department of Education are gratefully acknowledged. The

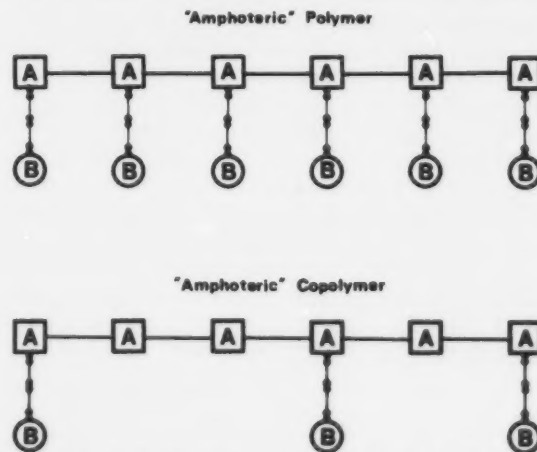


Fig. 1. Structure of "Amphoteric" polymer and copolymer.

numerous and helpful discussions of our colleagues, S. K. Roy and D. D. Patterson, are also acknowledged, with thanks.

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Discussion — L. E. St-Pierre

L. A. Utracki. Leon, it was not clear to me if these materials are blends or copolymers.

L. E. St-Pierre. Three of them are blends, which derives from the fact that a copolymer with a strong compatibility to one of the polymers is introduced into the mixture. All of these are compatible blends. The fourth is a blend of homopolymers. Here, we have too much siloxane character, even though the backbone is identical in the two polymers. So each of these samples is a physical blend. We have done all kinds of mixing and polymerizing. Blends of low-molecular-weight poly(dimethylsiloxane) fluids just do not go into PMMA. They are completely soluble as monomers but, after polymerization, they separate.

Without going into the enormous forces that Adi is working with, we postulated that, if we get the PMMA to interact with the backbone of this random copolymers, we could get compatibility. If it were a block ABA polymer, it would not be possible. But here, we have separation of probably half-a-dozen Å between the siloxane groups. There, we are asking: can we get enough interaction of the PMMA backbones to get some sort of blend? For the two homopolymers, the answer that nature is giving us is no. Now, the material used in the new contact lenses is not a blend but a copolymer. An interesting thing would be to study the nature of the gas diffusion. Why do we get a 20-fold increase in oxygen diffusion at 10 percent siloxane, relative to PMMA? Apparently, there is not a continuous path. I understand that Henry Schreiber is also working on this kind of thing.

L. A. Utracki. I believe that, in this particular case, the method of preparation must have a tremendous effect on the orientation morphology. The Strasbourg school demonstrated that, for block polymers, depending upon how the specimens are prepared, one gets a different morphology. For your mixtures, the method of preparation should also be important.

L. E. St-Pierre. We studied NMR only to get the composition. We analyzed these for composition through the hexamethyl disiloxane $-CH_3$ and the backbone methyl. We do not know whether this is a complete random copolymer. It seems that the siloxane group is far enough away from the double bond to have little effect on the copolymerization constants. From the other factors that you mentioned, we may have a block or a non-random copolymer.

H. P. Schreiber. We have not been looking at diffusion effects of the kind that you describe. I think that the pertinent point falls somewhere between what you were saying and what Leszek has just introduced into the conversation—namely, we have made membranes of poly(methyl methacrylate) and various acrylics copolymers. We prepare these by very different routes, including different solvent media, compression molding, and so on. To confirm what Leszek was saying, the transmission rates, the mass transfer rates, through these membranes are enormously dependent on the method of preparation. In fact, that turns out to be the most vital component; the composition is almost a second order.

L. E. St-Pierre. That does not surprise me. This is really the point that we have wondered about for a couple of years of looking in the literature for compositions of a new hard lens. For some of the samples, it is hard for me to conceive a 20-fold increase in the diffusion rate if the permeation had to go through the PMMA glass to a liquid microstructure of methyl siloxane and then through the glass again. What you are saying is that somehow we must have a continuous channel of PDMS or some modification, such as that where the T_g is way down at 226K, in order to get this kind of diffusion-rate increase.

K. C. Frisch. In connection with your very interesting work, it might possibly be of interest to study some copolymers of silicone with glycols. These are surfactants used for urethane foams and so on. They can be prepared with various degrees of hydrophilicity and other specific properties. They might produce interesting results as far as diffusion characteristics, viscosity, etc., are concerned.

L. E. St-Pierre. I shall dig out some of that work of yours and Jack Elliot's and see what is available. This has been a fun project. We are not yet looking at the normal things at all. We have even wondered about putting some of these samples on a Langmuir balance with silicone fluids as the floating medium. We know that they will be different from something like poly(acrylic acid) or poly(methacrylic acid). We have given the silicone group more freedom, moving it away from the backbone influence. Will this be sufficient? I do not know. Some of the commercial lenses have twice as much siloxane on the side chain. We can probably make a homopolymer with 70 percent, maybe even 80 percent of siloxane mers to enhance the diffusion.

Some Solid-State Properties of Blends of Polyethylene Terephthalate and Polyamide-6,6

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Polymer blends incorporating polyamide-6,6 (PA) and polyethylene terephthalate (PET) and having the following PA wt.% concentrations were prepared: 0, 5, 10, 25, 30, 35, and 100. Samples were obtained by molding in a reciprocating-screw injection-molding machine. The samples were annealed to minimize frozen-in stresses without increasing the crystallinity level in the material. Melting and heat-of-fusion data, obtained with the differential scanning calorimeter, suggest an overall increased crystallinity in the blends, as indicated by a significant excess heat of fusion. Whereas the neat polymers exhibit ductile failure under both tensile and impact testing conditions, the blends show brittle behavior. Finally, the abrasion resistance of the blends is inferior to that observed for PET but higher than the resistance of PA.

INTRODUCTION

Polymer blends are prepared in order to improve some specific properties of finished articles (1). Various aspects relating to the behavior and economics of polymer blends have been discussed by other workers (2-4). In particular, the subjects of rheology and morphology of polymer blends have received special attention recently (5-13). In an earlier work, Utracki, *et al.* (14-19), have studied the melt rheology of blends of poly(ethylene terephthalate), PET, with poly(amide-6,6), PA. Their results indicated the presence of a degree of association and/or cocrystallization involving these two polymers.

PET and PA are semicrystalline polymers. Their degree of crystallinity can be controlled to a certain extent by processing conditions: viz., thermo-mechanical history, including cooling rate and annealing. Crystallinity has a great influence on the ultimate solid-state properties such as density, optical clarity, tensile and impact strength, etc. Separately, PET and PA have been exhaustively studied as films, sheets, and fibers. In this article, we discuss the properties of the blends. Some mechanical and surface properties of these blends are presented here for the first time. The work

is a natural extension of the previous examination of the melt behavior. The present work should provide information on the suitability of these materials for specific applications.

EXPERIMENTAL

Materials

KODAPAK 7352 (supplied by Eastman Kodak) and ZYTEL 42 (obtained from E. I. DuPont de Nemours and Co.), were the PET and PA resins, respectively, that were employed in this study. The properties of these resins are listed in Table 1. Five blends were prepared employing the above resins. As described below, injection molding was employed in the preparation of the blends. Data relating to the composition and ap-

Table 1. Properties of Pure Materials as Quoted in Commercial Literature

Commercial Name Symbol	M _n	M _w /M _n	Melting Point T _m (°C)	Softening Point (°C)	Melt Viscosity at 275°C (poise)
Kodapak 7352 (PET)	55,000	2.2	257	245	—
Zytel 42 (PA)	36,000	—	258	—	25,000

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pearance of the injection-molded samples are given in Table 2.

It is well-known that both PET and PA are quite hygroscopic and that the absorbed moisture has a plasticating effect, particularly strong on PA (20). For this reason, all the samples were prepared in the same manner (see below), which would eliminate the effect of moisture. Furthermore, before mechanical testing, all moldings were dried and annealed under identical conditions of temperature and time.

Preparation of Moldings

The detailed procedure is described as follows. First, the resins were dried—PET for 72 h at 135°C and PA for 72 h at 85°C—under reduced pressure of 1.66 KPa. About 3 kg of dried resin, combined in the desired proportions, were loaded into the double-cone mixer. Mixing was carried out at a shaft speed of 40 rpm and an inside bar speed of 900 rpm for 10 min. Then, the dry-blended resins were transferred into the hopper of a 68-ton, reciprocating-screw, Metalmec injection-molding machine. Before each run, the machine was purged with high-density polyethylene (EX2 2908) and, subsequently, with about 1 kg of the material to be molded. Only after that were the samples collected. All the moldings were prepared under identical conditions, as given in Table 3. The geometry of the samples is shown in Fig. 1. The samples were stored at ambient temperature in sealed plastic bags for up to three months before testing.

Post-Molding Treatment

In order to relax the frozen-in stresses (21, 22) present in the quenched moldings, all samples were annealed. The PET samples were taken as reference, since they were transparent and since PET constituted the major component of the blend.

Table 2. Composition and Appearance of Moldings Employed in the Study

Material Code	PET/PA Compositions (wt.%)	Appearance of Injection-Molded Samples
1	100/0	Transparent
2	95/5	Translucent (greenish color)
3	90/10	Translucent (greenish color)
4	75/25	Opaque (light green)
5	70/30	Opaque (light green)
6	65/35	Opaque (greenish cream)
7	0/100	Opaque (cream color)

Table 3. Injection-Molding Conditions

Barrel Temperatures:	
Front Zone	290°C
Rear Zone	220°C
Injection time:	4 s
Holding time:	24 s
Injection-pressure range (in mold):	
Filling	45-55 bars
Packing	130-150 bars
Injection velocity:	1.8 cm/s
Mold cooling water temperature	18 (±2)°C

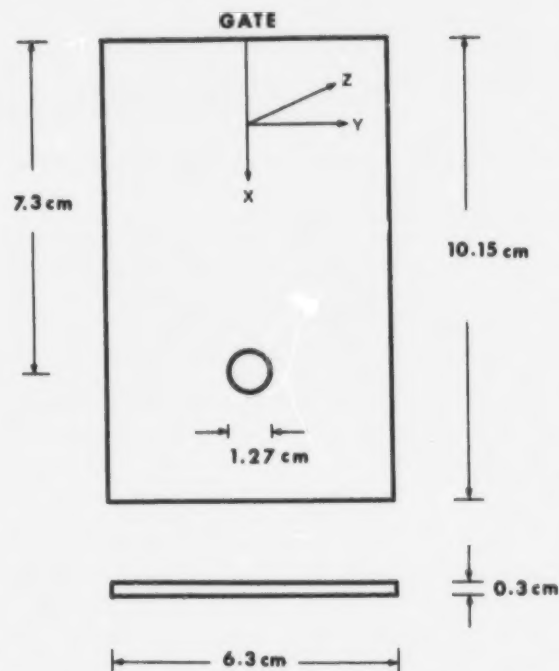


Fig. 1. Geometry of the injection-molded samples.

To ensure that frozen-in stresses have been relaxed, birefringence was measured before and after annealing. Firstly, birefringence was measured at various points in the x-y plane (see Fig. 1) using a polarized light microscope (Reichert Austria, model Nr. 345 054, and Compensator Drenkompensator Quartz model CARL ZEISS). Next, the samples were annealed at temperature, $T \geq T_g$ for a specific time, and the birefringence was remeasured. The following temperatures and times were used, respectively: $T = 70^\circ\text{C}$, $t = 8$ h; $T = 75^\circ\text{C}$, $t = 24$ h; $T = 80^\circ\text{C}$, $t = 12$ h, and $T = 80^\circ\text{C}$, $t = 24$ h. After several trials, the annealing conditions, which led to reduction, but not complete elimination, of birefringence of the samples, were established. The birefringence of injection-molded samples before annealing ranged from $8.66 \cdot 10^{-4}$ to $15.3 \cdot 10^{-4}$ and, after annealing, from $0.35 \cdot 10^{-4}$ to $2.48 \cdot 10^{-4}$. The residual birefringence is probably related to the variation in thickness. On the basis of the above procedure, the annealing conditions were established at $80^\circ\text{C} \pm 1$ for 24 h under the pressure of 1.66 KPa. In order to avoid hydrolysis, the samples were dried at 50°C for 8 h at 1.66 KPa prior to annealing. Under these annealing conditions, there was no apparent change in crystallinity. Before mechanical testing, all samples were preconditioned according to ASTM D 618 (group A) procedure at ambient conditions of 23.3°C 50 percent R.H. for 48 h. All tests were carried out at conditions comparable to those employed for preconditioning.

DSC Tests

A Perkin-Elmer Differential Scanning Calorimeter, DSC-1, and aluminum pans were used. Thin flakes (5 to 6 mg) were carefully cut from the annealed moldings

in order to avoid shear-induced crystallization. These were used as DSC test samples. The machine was calibrated for both power and temperature close to the temperature of interest. The standard indium and tin samples were used for calibration. Both calibration and testing were carried out at the constant scanning rate of 20°/min. Prior to scanning, the test samples were allowed to equilibrate at the starting temperature for 2 min. Separate tests were performed for heat of fusion, ΔH_f , and melting point, T_m , determination.

Tensile Tests

The tensile tests were carried out according to the standard ASTM D-638 method. The geometry of the test samples used was as per the recommendations of group (IV) specimen dimensions, under the same ASTM designation. Two tensile test samples were milled from one molding with the help of a guide. The samples thus prepared were annealed and preconditioned. All the tests were performed employing Instron Tensile Tester Model 1123 in conjunction with Instron Environmental Chamber Model A74.

Impact Tests

Rheometrics High-Rate Impact Tester Model RIT-8000 was employed in conjunction with Rheometrics Environmental Chamber Model EC-6020. This Impact Tester is a controlled-velocity device in which a probe impacts the test specimen (unnotched sheet or film) and drives through at a preselected speed. The force-deflection curve is immediately displayed on the built-in computer screen. The data points on the curves are selected by the operator, and a hard copy of the graph is obtained. Also, the built-in printer provides some numerical data. A schematic of the impact assembly is shown in Fig. 2. The impact speeds employed were 1.27, 8.89, 20.32, 38.1, and 381 m/min.

Abrasion Tests

The abrasion tests were performed according to ASTM Standard D-2142 requirements. The equipment used was Dual Abrasion Tester Model 505. The abrasant employed were CALIBRADE H-18 of Teledyne Taber. All samples were abraded for 1,000 cycles under a constant weight of 2.26 kg. The resulting loss of weight was noticed. For the purpose of calculating the loss of volume corresponding to the loss of weight, the densities of annealed samples were measured using a specific gravity bottle and liquid meriam-100, under laboratory conditions of 23.3°C.

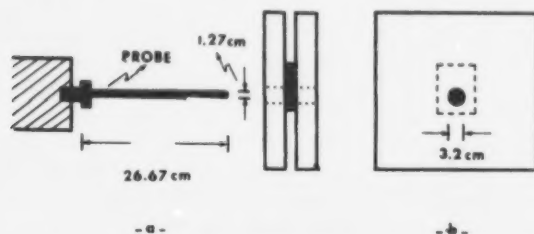


Fig. 2. The impact test arrangement: (a) ram-probe-clamp assembly; (b) the side view.

RESULTS AND DISCUSSION

Melting Point

The DSC tests were performed for the determination of melting point, T_m , of annealed PET, PA, and blends. The test samples were heated from 270 to 560 K; six repetitive runs were conducted. The melting behavior of all the materials is shown in Fig. 3. The T_m s, read as the average values of the endotherm peak, are shown in the last column of Table 4. The T_m values of PET and PA are comparable to those reported by other workers and are summarized in the references (14). However, there is a significant difference in the nature of fusion curves when compared to the earlier measurements (14). All of the annealed samples of blends show the peak broadening, unlike the earlier results, where two separate distinguishable peaks were obtained. The peak broadening increases with the increase of PA content; the peak of blend #6 has almost a flat top. The new results, showing one instead of two peaks, are probably due to better mixing and annealing.

The melting points obtained from both studies are shown in Fig. 5. The T_m values for PET and PA were found as 250.6° and 263°C against the previous values of

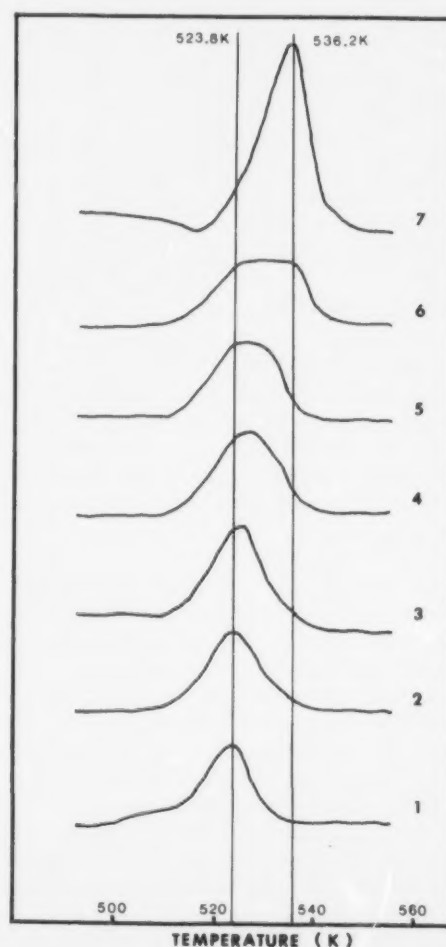


Fig. 3. DSC scanning curves at 20°C/min; for PET, 1; PA, 7; and Blends, 2-6.

Table 4. Summary of DSC Data

Material	ΔH_c cal/g	S	ΔH_f cal/g	S	$\overline{\Delta H_f} = \Delta H_f - \Delta H_c$ cal/g	S	Δh cal/g	Estimated Blends Crystallinity 'x' ($\Delta H_f/\Delta H_f$) 100	T_m (°C)
1	5.39	0.50	6.55	0.72	1.16	0.10	0	4.0	250.6
2	5.55	0.83	7.98	0.72	2.43	0.22	0.80	7.7	251.8
3	5.28	0.51	8.33	0.67	3.06	0.07	1.00	9.5	251.9
4	3.81	0.43	8.69	0.68	4.88	0.37	1.40	14.7	254.9
5	3.58	0.10	8.35	0.15	5.77	0.05	1.80	17.9	257.4
6	3.08	0.13	8.35	0.71	5.27	0.79	0.90	15.1	260.9
7	—	—	10.45	0.53	10.45	0.53	0	23.2	263.1

S = Standard deviation.
All properties represent average values.

249.5° and 265°C, respectively. The increase in the T_m values of PET and blends may indicate a small increase in the initial crystallinity during injection molding (23). It should be noted that the glass transition temperature, T_g , changes with crystallinity, x and, for $x \approx 4.0$ percent, one may expect that $T_g = 77^\circ\text{C}$ (24). Besides, it has been reported (29) that, at annealing temperatures, $T_a \leq 90^\circ\text{C}$ PET does not crystallize, but the molecules simply orient themselves to prepare for crystallization at $T_a > 90^\circ\text{C}$. The 1.6°C lower value of T_m determined in this work for PA may reflect the lower crystallinity of the samples. It should be pointed out that, in the past, several authors reported double melting points for PET (23, 26, 27). The presence of two peaks was usually observed for higher crystallinity (x) samples, annealed and crystallized at higher temperatures, 140° to 240°C. In this work, the higher crystallinity for the blends was achieved by the presence of the nucleating agent (PA). If so, the explanation for double T_m may relate more to the nature of PET melting behavior than to the mixed PA/PET crystal theory (14).

Crystallinity and Fusion

There are various methods (x-ray diffraction, density measurements, etc.) to determine crystallinities of semicrystalline PET (28-31) and PA (32, 33). In this study, the percent crystallinity, X , is defined as the wt. % of the crystalline phase present in the semicrystalline polymer, as calculated from the heat of crystallization (ΔH_c) and fusion (ΔH_f). All the samples were heated at a constant heating rate from 316 to 550 K. Results obtained on specimens cut from different positions were reproducible, suggesting that fast-sample size was significantly larger than domain size.

PET and all the blends showed crystallization exotherms followed by fusion endotherms, as shown in Fig. 4. The heat of fusion of the crystals originally present in the samples ($\overline{\Delta H_f}$) was calculated as the difference between the two transition energies; i.e., $\overline{\Delta H_f} = \Delta H_f - \Delta H_c$. This method was previously employed by other workers (28). The two transition peaks for low crystallinity PET were reported by several workers (29, 24-26). The DSC results of this work are presented in Fig. 4. The reason for the exotherm in the case of PET is due to the fact that the rate of crystallization is very high at some narrow range of temperature between 90° and

140°C (23). In the present study, it has been found that the peak crystallization temperature (T_c) of PET is 140.8°C. The T_c for blends is lower, 133.8° to 135.8°C. Thus, the presence of PA nuclei seems to facilitate the crystallization of PET.

The heat of fusion ($\overline{\Delta H_f}$), calculated as outlined above, is given in Table 4. The crystallinity, x , was calculated as follows:

$$x = (\overline{\Delta H_{fPET}}/\Delta H_{f(PET)}) 100 \text{ for PET}$$

$$x = (\Delta H_{fPA}/\Delta H_{f(PA)}) 100 \text{ for PA, and}$$

$$x = [(\Delta h(100)/(100 - c) + (\overline{\Delta H_{fPET}})/100)]$$

for blends,

where $\overline{\Delta H_{fPET}}$ and $\overline{\Delta H_{fPA}}$ are the heats of fusion of crystals originally present in samples of pure PET and pure PA, respectively. $\Delta H_{f(PET)} = 31.8$; $\Delta H_{f(PA)} = 45.0$ (cal/g) are the values of heat of fusion, theoretically estimated for 100 percent crystalline PET (34) and PA (30, 35), respectively. The excess heat of fusion, Δh , for the blends was calculated as:

$$\Delta h = \overline{\Delta H_f} - [c \overline{\Delta H_{fPA}} + (100 - c) \overline{\Delta H_{fPET}}]/100$$

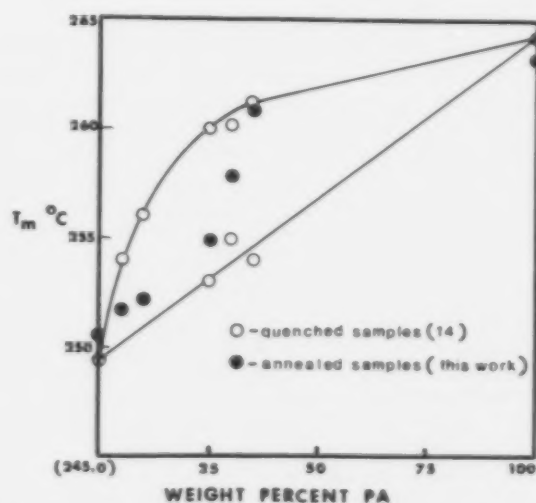


Fig. 4. DSC heating curves at 20°/min; for PET, 1; PA, 7; and Blends, 2-6.

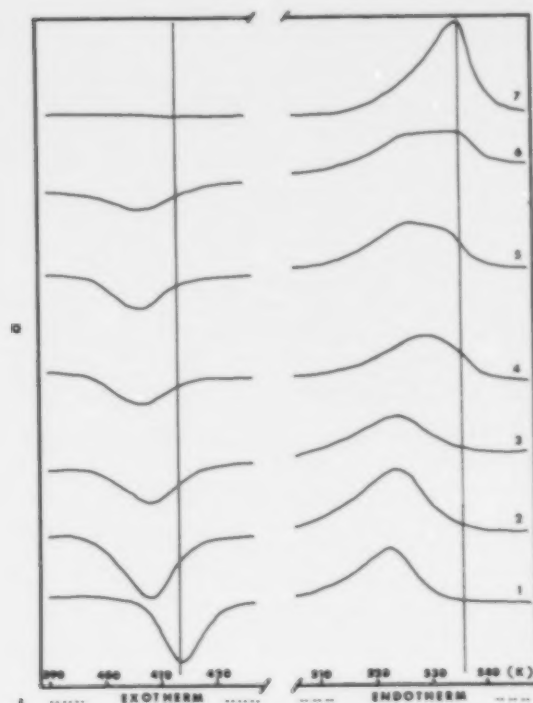


Fig. 5. Comparison of T_m vs. composition for PET, PA, and the Blends.

where ΔH_f is heat of fusion of blend of composition, c , where c is concentration of PA in wt. %.

The values of x , calculated for the pure polymers, are 4 and 23.2 percent for PET and PA, respectively. The ΔH_f is plotted as a function of mole% PA (x_{Am}) in Fig. 6. It is apparent that the addition of PA, at $x_{Am} \leq 45$ percent, enhances the crystallization of PET. The effect is visible even for $x_{Am} \leq 7$ percent; i.e., in the concentration range in which the PA is soluble in PET (14-19). ΔH_f for $x_{Am} = 45$ percent scatters widely. In fact, the results may be grouped into two "subaverages"—one lying on the curve defined by the other four blends, the second on the straight line connecting the neat resins (ΔH_f) points. This is better seen in Fig. 7, where the excess heat of fusion, Δh , as defined before, is plotted as a function of x_{Am} . Δh may

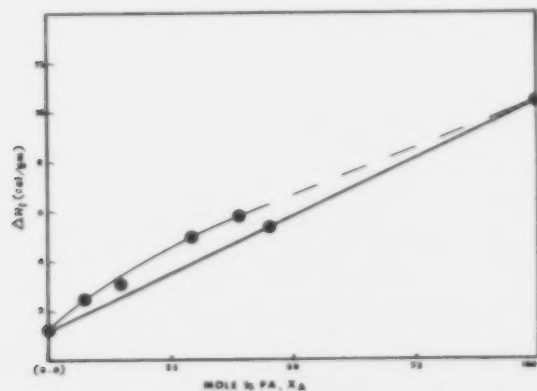


Fig. 6. Heat of fusion, ΔH_f , of PET, PA, and the Blends vs. mole% PA, x_A .

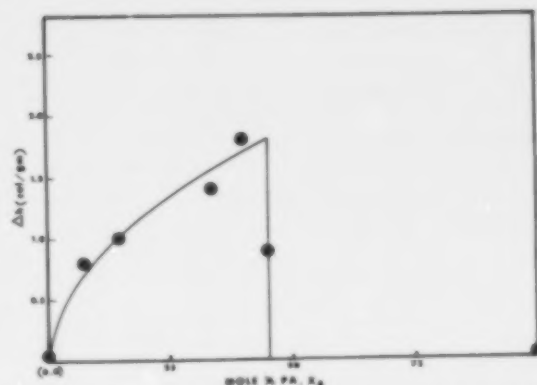


Fig. 7. The excess heat of fusion, Δh , as a function of mole% PA, x_A .

be considered as reflecting the increased crystallinity observed in the blends, as a result of blending, beyond the levels existing in the neat resins. One may expect that, below $x_{Am} = 45$, the continuous phase is PET, and the dispersed phase is PA (with the higher T_m), which acts as a nucleating agent. In the higher range of x_{Am} , PA forms a continuous phase and, because of the reduction of the interfacial area, it becomes less efficient in nucleating PET. Assuming that Δh is related to the excess crystallinity of PET only, the total crystallinities of blends may be calculated (see Table 4).

Tensile Properties

Various reports regarding the tensile properties of several polymers and blends are available (37-42). We have tested the tensile properties of PET, PA, and blends at a constant strain rate of 5 mm/min. The actual load-elongation curves are reproduced in Fig. 8. The results are summarized in Table 5.

The pure polymers show ductile behavior; i.e., yield followed by plastic deformation until break. The blends, as expected, exhibit brittle behavior, and there are no signs of necking. Figure 9 shows the stress-strain diagram for all materials until yield or break, whichever comes first.

In Fig. 10, the maximum force (the yield force in case of pure resins and break force in case of all blends) is

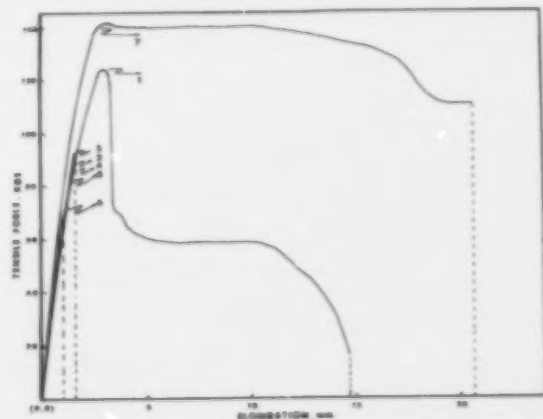


Fig. 8. Tensile load-elongation curves for PET, 1; PA, 7; and Blends, 2-7.

Table 5. Tensile Properties of PET, PA, and Blends at Strain Rate of 5 mm/min

Material	Yield Force 'KG'	S	% Strain at Yield	S	Breaking Force 'KG'	S	% Strain at Break	S	Tensile Modulus (kg/cm ²)	*Tensile Strength (at Yield or Break) kg/cm ²	S
PET	125	2	11.4	0.2	17	2	57.7	13.4	8400	690	40
2	—	—	—	—	86	13	6.5	1.4	8500	490	40
3	—	—	—	—	83	17	6.2	1.4	8500	460	90
4	—	—	—	—	86	16	6.0	1.4	9400	480	90
5	—	—	—	—	92	4	6.3	0.4	9400	510	40
6	—	—	—	—	71	6	4.6	0.4	9400	390	40
PA	140	6	12.3	0.2	113	4	73.2	6.9	9400	770	30

S = Standard deviation.

All properties represent average values.

* Tensile strength calculated for pure polymers (ductile) at yield and for blends (brittle) at break.

shown as a function of PA concentration, *C*. Pure resins show higher values of maximum force (F_{max}); i.e., 124.75 and 139.75 kgs for PET and PA, respectively. The same force for the blends is much lower and appears to be somewhat insensitive to the concentration of PA in the blend. The tensile strength, calculated as the value of F_{max} divided by the original area of cross-section of samples, is plotted against PA concentration in Fig. 11. The variation of percent elongation at break with PA concentration is depicted in Fig. 12. These results suggest that the effect of blending is to reduce the

tensile strength and to cause the embrittlement of the samples.

Impact Properties

The impact properties of plastics are measured by a variety of techniques, including Izod, Charpy, falling weight, and high-speed torpedo methods (43-50). In the first two methods, both notched and unnotched specimens are used, but these methods are not useful for films and thin plastic sheets. The use of notched samples, while permitting impact testing of samples

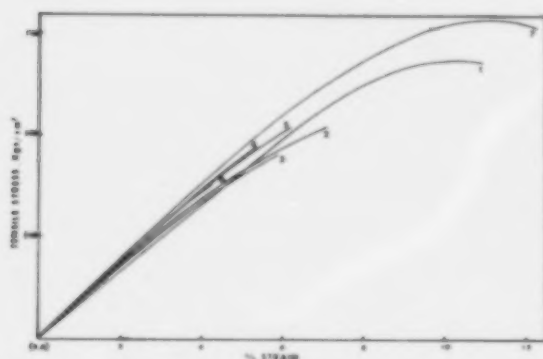


Fig. 9. Tensile stress-strain diagram of PET, 1; PA, 7; and Blends, 2-6. Samples pre-conditioned at 23.3°C.

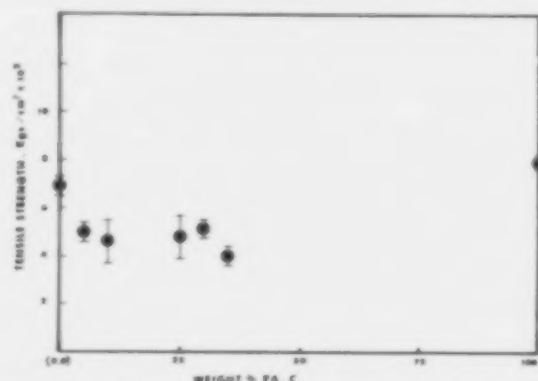


Fig. 11. Tensile strength as function of PA concentration, *C*.

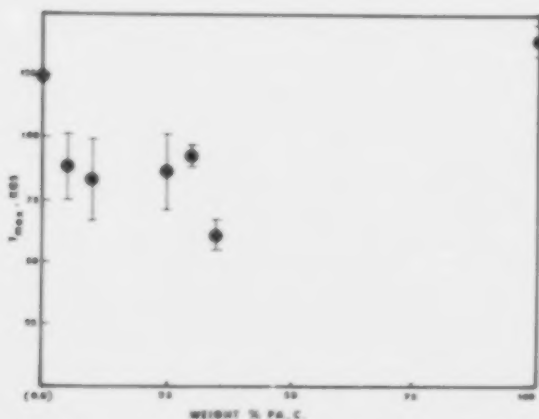


Fig. 10. Maximum tensile force, T_{max} , as a function of PA concentration, *C*.

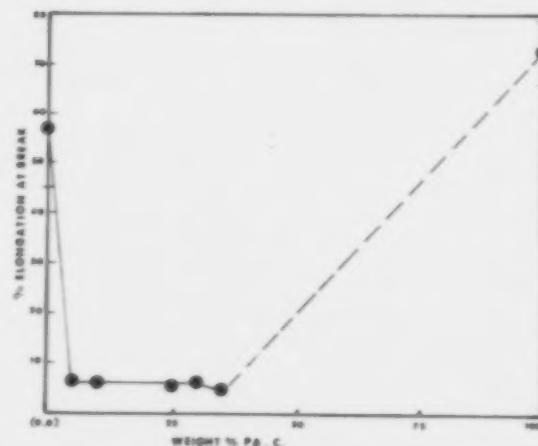


Fig. 12. Elongation at break as a function of PA concentration, *C*.

employing practical loads, could lead to stress localization at the notch (43). Thus, fracture becomes biased toward crack propagation rather than crack initiation. The present study has employed a new, high-speed, linear-impact test based on the use of a newly introduced tester by Rheometrics, Inc.

The results of the impact tests, which are summarized in Tables 6 to 10, show that, for the neat polymers,

the F_{max} value increases with the impact speed (by about 50 percent within the investigated range). On the other hand, the F_{max} values for blends are very low and remain approximately constant, independent of composition and speed. Similarly, the initial moduli for the blends are low, virtually independent of composition and speed. These results are probably the consequence of the increased crystallinity of the PET matrix upon ad-

Table 6. Impact Properties of PET, PA, and Blends at Impact Speed of 1.27 m/min

Material	Force (kg)				Deflection (mm)				Energy (absorbed) Joules				Modulus (kg/mm)	S
	Yield	S	Break	S	Yield	S	Break	S	Yield	S	Break	S		
PET	319	18	225	17	7.4	0.7	19.9	1.4	11.3	0	41.0	3.5	51	5
2	—	—	82	16	—	—	3.1	0.5	—	—	≤1.1	—	24	4
3	—	—	122	8	—	—	4.0	0.4	—	—	≤1.5	0.5	26	1
4	—	—	82	9	—	—	2.8	0.4	—	—	≤1.1	—	24	2
5	—	—	71	8	—	—	2.6	0.4	—	—	≤1.1	—	21	4
6	—	—	74	14	—	—	3.0	1.1	—	—	≤1.1	—	13	7
PA	556	23	314	43	8.5	0.1	18.5	2.3	24.4	2.4	61.7	6.7	75	1

S = Standard deviation.
All properties represent average values.

Table 7. Impact Properties of PET, PA, and Blends at Impact Speed of 8.89 m/min

Material	Force (kg)				Deflection (mm)				Energy (absorbed) Joules				Modulus (kg/mm)	S
	Yield	S	Break	S	Yield	S	Break	S	Yield	S	Break	S		
PET	379	19	183	13	7.8	0.5	18.5	1.2	15.0	1.5	46.6	2.6	57	3
2	—	—	86	20	—	—	3.5	1.1	—	—	≤1.1	—	20	8
3	—	—	109	24	—	—	4.3	0.9	—	—	≤1.8	0.5	18	8
4	—	—	82	14	—	—	3.6	1.3	—	—	≤1.1	—	19	6
5	—	—	74	6	—	—	2.8	0.1	—	—	≤1.1	—	17	2
6	—	—	67	11	—	—	2.9	1.2	—	—	≤1.1	—	16	7
PA	624	11	254	47	9.2	0.5	16.3	2.2	30.5	1.1	62.5	6.1	84	2

S = Standard deviation.
All properties represent average values.

Table 8. Impact Properties of PET, PA, and Blends at Impact Speed of 20.32 m/min

Material	Force (kg)				Deflection (mm)				Energy (absorbed) Joules				Modulus (kg/mm)	S
	Yield	S	Break	S	Yield	S	Break	S	Yield	S	Break	S		
PET	390	22	140	8	7.4	0.6	19.6	1.0	15.0	1.5	53.1	2.6	62	3
2	—	—	77	16	—	—	3.0	0.4	—	—	≤1.1	—	16	3
3	—	—	86	20	—	—	3.2	0.7	—	—	≤1.1	—	21	6
4	—	—	78	20	—	—	3.0	0.6	—	—	≤1.1	—	17	2
5	—	—	72	9	—	—	3.0	0.4	—	—	≤1.1	—	20	6
6	—	—	69	12	—	—	3.0	0.4	—	—	≤1.1	—	17	6
PA	685	0	229	16	9.1	0.2	18.8	0.8	31.2	3.2	77.2	3.4	92	2

S = Standard deviation.
All properties represent average values.

Table 9. Impact Properties of PET, PA, and Blends at Impact Speed of 38.1 m/min

Material	Force (kg)				Deflection (mm)				Energy (absorbed) Joules				Modulus (kg/mm)	S
	Yield	S	Break	S	Yield	S	Break	S	Yield	S	Break	S		
PET	425	15	141	12	7.9	0.6	19.9	0.9	18.0	0	55.7	3.4	64	4
2	—	—	54	15	—	—	2.5	0.7	—	—	≤1.1	—	18	4
3	—	—	86	12	—	—	3.3	0.6	—	—	≤1.1	—	19	3
4	—	—	75	13	—	—	3.0	0.4	—	—	≤1.1	—	21	2
5	—	—	66	12	—	—	2.9	0.5	—	—	≤1.1	—	17	2
6	—	—	78	17	—	—	3.0	0.4	—	—	≤1.1	—	20	2
PA	703	9	292	23	9.1	0.7	17.3	1.1	32.3	2.7	72.3	5.1	97	2

S = Standard deviation.
All properties represent average values.

Table 10. Impact Properties of PET, PA, and Blends at Impact Speed of 381 m/min

Material	Force (kg)				Deflection (mm)				Energy (absorbed) Joules				Modulus (kg/mm)	S
	Yield	S	Break	S	Yield	S	Break	S	Yield	S	Break	S		
PET	496	16	161	15	7.7	0.5	20.8	1.1	19.2	1.1	62.8	4.1	57	1
2	—	—	60	6	—	—	3.4	0.6	—	—	≤1.1	—	10	3
3	—	—	65	6	—	—	3.1	0.5	—	—	≤1.1	—	15	2
4	—	—	66	9	—	—	3.1	0.5	—	—	≤1.1	—	16	2
5	—	—	62	10	—	—	3.7	0.8	—	—	≤1.1	—	21	7
6	—	—	54	9	—	—	2.5	0.5	—	—	≤1.1	—	24	2
PA	773	19	311	86	8.9	1.0	16.3	1.4	43.7	2.7	74	6.7	85	6

S = Standard deviation.

All properties represent average values.

dition of PA. In fact, we have observed that pure PET, when allowed to crystallize to a higher degree of crystallinity $\alpha \geq 8$ percent, exhibits impact performance similar to that of blends. Therefore, like neat PET, these blends should not be used in the unoriented state; the high degree of brittleness would reduce their utility. The above conclusions are further illustrated in Figs. 13 to 16.

Abrasion Resistance

The abrasion resistance of a solid body is defined according to ASTM 1242-56 specification as follows: "The ability of the solid body to withstand the progressive removal of material from its surface as the result of rub-

bing, scrapping, or erosive nature." A review of the types and test methods of abrasion measurement techniques is available (51). In the present study, the samples were tested with Teledyne Taber H-18 under a constant weight and for constant time. The resulting losses of weight and volume are presented in Table 11. The volume loss is plotted vs. the composition in Fig. 17. The abrasion results show that there is a trend of decreasing abrasion resistance with increasing PA concentration, C , for $C \leq 30$ percent. In spite of the poor reproducibility of the results, it appears that the abrasion resistance of the blends is somewhat lower than for the pure PET. One of the reasons contributing to the poor reproducibility of data was that the width of the

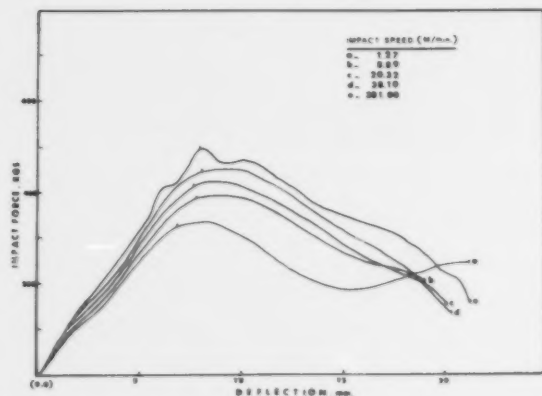


Fig. 13. Impact force-deflection curves for PET.

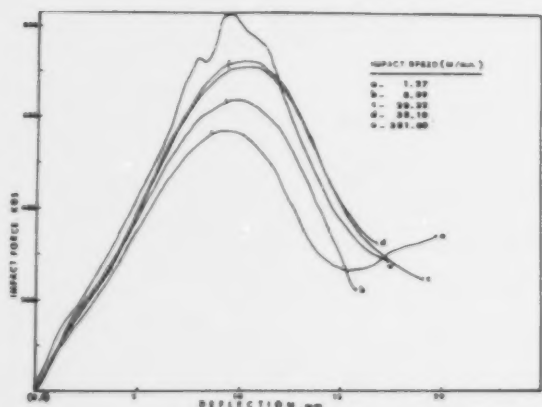


Fig. 14. Impact force-deflection curves for PA.

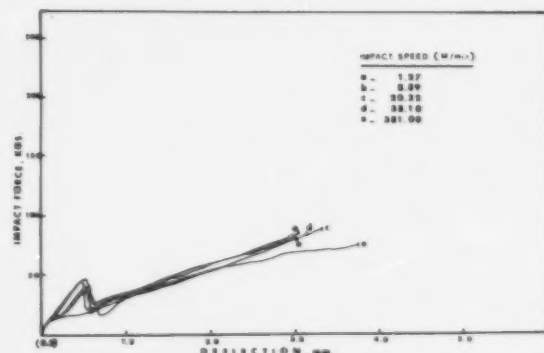


Fig. 15. Impact force-deflection curves for Blend-4.

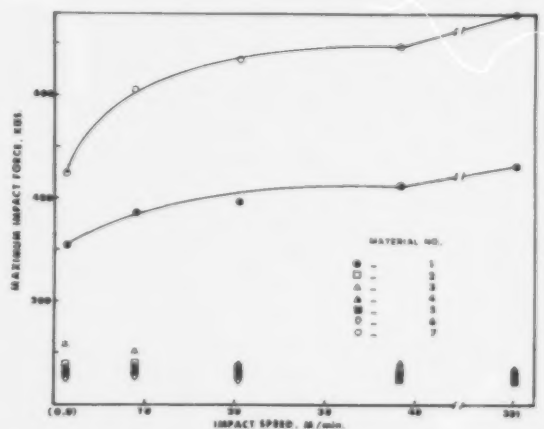


Fig. 16. Maximum impact force as a function of impact speed for PET, 1; PA, 7; and Blends, 2-6.

Table 11. Summary of Abrasion Results

Material	Density ' ρ ' g/cm ³		Weight loss g		Volume loss cm ³	
		S		S		S
1	1.416	0.011	0.0135	0.0022	0.009	0.003
2	1.400	0.017	0.0196	0.0064	0.014	0.005
3	1.341	0.019	0.0174	0.0050	0.012	0.005
4	1.288	0.007	0.0151	0.0053	0.012	0.003
5	1.266	0.004	0.0126	0.0025	0.010	0.002
6	1.255	0.003	0.0274	0.0054	0.022	0.004
7	1.192	0.016	0.0332	0.0654	0.028	0.004

S = Standard deviation.
All properties represent average values.

specimens employed in the present study was smaller than that specified by the standard procedure. Consequently, the abrading wheel did not rest completely on the body of the specimen.

CONCLUSION

The results of the work reported above suggested that PET and PA exhibit a certain degree of compatibility in the molten state, which permits the preparation of finished articles from the blends by means of a process like injection molding. Such articles have acceptable mechanical integrity and appearance.

Most of the observations can be associated, to some extent at least, with the enhanced crystallinity of PET in blends, especially up to a concentration of polyamide around 35 percent. In the unoriented state, the blends exhibit brittle failure under both tensile and impact testing conditions. On the other hand, the neat polymers exhibit ductile failure. Due to the brittle nature of the blends, they probably would not be very useful in the unoriented form, especially if the mechanical properties of the finished articles are important.

ACKNOWLEDGMENTS

The authors would like to express their thanks to the Natural Science and Engineering Council of Canada, the Ministère de l'Éducation, Gouvernement du Québec, the Industrial Materials Research Institute of the National Research Council of Canada, and McGill University for financial support to carry out the work described in this article.

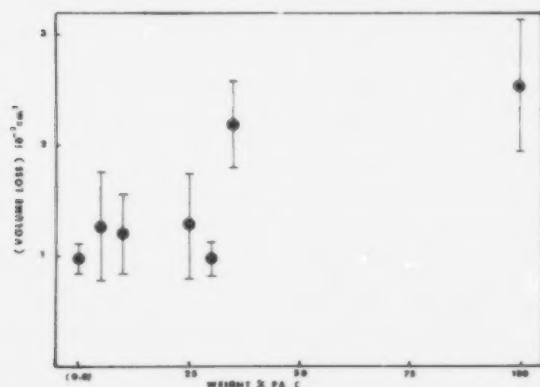


Fig. 17. Abrasion resistance (loss of volume) plotted against PA concentration, C.

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Discussion—M. A. Sahto

V. di Tullio. At the beginning of your lecture, you said that you prepared the samples and let them stand around for three months. Was there a specific reason for that or did you simply not have time to do the work?

M. A. Sahto. We wanted to prepare all the samples and test them together to ascertain the reproducibility.

V. di Tullio. Did you ever witness any aging effects?

M. A. Sahto. We did not get to that as yet.

G. L. Bata. On Fig. 7, when you correlate the excess crystallinity to compositions, you have a very "courageous" curve that comes down to zero. Do you have any explanations, any reason backing out this graph?

M. A. Sahto. Yes. We saw that PA nucleates PET crystallization. At the concentration of 35 wt. % of PA, or 45 mol%, the system is no longer able to nucleate PET any further. At that concentration, we have much greater fluctuation of data. Depending on the sample, the value near top or near zero heat of fusion was determined at that point. I think that, if we had a higher composition, probably the excess heat would be zero.

L. A. Utracki. I would like to add to this response. The reason why we drove this curve this way is related to the assumed mechanism for extra nucleation of poly(ethylene terephthalate) by polyamide. When polyamide is dispersed, it provides nucleating centers for PET. As a result, one gets enhanced crystallization. One sees this, not only as excess heat of fusion, but also in the shift of the crystallization temperature. The picture is consistent. However, once the PA content exceeds about 45 mol%, it no longer constitutes a dispersed phase. It is not complete phase reversal but a transition region where both phases intermix. It seems that the total interphase surface is drastically reduced. At still higher concentrations, the PET is the dispersion phase in polyamide. It is absurd to expect that, when the mechanism is reversed, PET crystallizes at much lower T than PA, so it does not have any nucleating effect. So we would expect that, at these concentrations, one would have a linear increase of total crystallinity; i.e., excess heat of fusion should be zero. In other words, only in the initial part of the curve will the nucleation effect be present.

R. S. Porter. Beautiful. The point is that it is not the absolute concentration that is important, but the relative surface area. Therefore, one can indeed nucleate one by the other, with the scale being surface area rather than concentration. Further to this point is that the design of that interphase is crucial to the impact in mechanical properties. I can conceive that your blend sys-

tem is near ideal for doing this. For example, you can control the crystallization. Indeed, you can adjust the cocrystallization temperature and the surface area. You have the option to crystallize PET on Nylon or go above the melting point of the PET and reverse it—crystallize the Nylon upon the amorphous PET. So, potentially, you have ways to control the interface from both sides by the temperature and conditions of crystallization. I would envision that, for a certain specific ratio of polymers, you might get quite different results.

L. A. Utracki. I would like to underline the principles for designing these experiments. We wanted first to get a completely amorphous PET with all the residual stresses relaxed. Next, we kept the conditions constant so as to observe the cocrystallization or the extranucleation mechanisms, in order to distinguish between them. I would like to add one additional point of information. During the previous work on rheology of melt, we had a very definite indication of chemical reaction between amide and ester groups. However, according to rheological studies, this reaction requires about 20 min of heating at about 290°C. In other words, it is a very slow reaction. The system is marvelous to play with. It not only allows you to adjust the morphology from the point of view of the crystallization, but also from the point of view of interphase interactions. One can conduct the reaction further and generate a more extensive intermixing. The problem is the lack of time.

R. E. Prud'Homme. You mentioned that you had some evidence for the presence of cocrystallization between PT and Nylon. I was very surprised by this comment. We have tried to find a system where cocrystallization between polymers was possible, both in the literature and from our own work. Just to give one example, poly(caprolactone) is completely miscible with poly(vinylidenechloride). This is conducted from measurements of the glass transition temperatures by dynamic mechanical methods, and so on. However, despite the miscibility between those two polymers in the amorphous phase, it is very clear from X-ray diffraction that we have PVCL₂ crystals and poly(caprolactone) crystals without any interference between the two. I am not aware of any system cocrystallization that would show.

M. A. Sahto. I was referring to the comment in the previous work done by Utracki. He would be in a better position to explain.

L. A. Utracki. First of all, there are isomorphic polymer crystals. Cocrystallization is a rare but known phenomenon. For instance, there are few systems listed in the Olabisi, Robeson, and Shaw book on "Polymer-Polymer Miscibility." This is one answer. We postulated cocrystallization on the basis of the unusual drift of the melting point with composition, reported for annealed samples in the first part of this study, which will appear in the July issue of *J. Appl. Polym. Sci.* We postulated the formation of cocrystals between polyamide and poly(ethylene terephthalate) on the basis of DSC results. From the data on the mechanical properties of the samples prepared by the quenching mechanism, reported today, I think that the indications are rather con-

trary to the cocrystallization mechanism. However, I do not think that the response is clear, no.

T. M. Malik. You used two polymers, Nylon and PET, both being slightly crystalline. In studying the mechanical properties of polymers, I believe that the glass transition temperature has much to do with mechanical properties. Definitely, these properties depend on glass temperature. It seems to me that you have measured all samples at one temperature, and thus, definitely excluded the transition region or transition effects. Did you ever try to measure these properties at one temperature where the glass transition temperature has equal effects on all blends and homopolymers?

M. A. Sahto. Actually we have tried two more temperatures. I cannot say anything definite but, at all temperatures, the phenomena look similar.

L. A. Utracki. The glass transition temperatures for PET and PA are about 60° to 70°C. For the blends, due to high crystallinity, we did not manage to determine T_g , but I do not see any reason to expect that suddenly

their T_g s would follow the ambient temperature of the measurements. We consistently operate within the glass region where the relative temperature effect is small.

G. Sourour. In Dr. Kamal's laboratory, some orientation study on polyethylene was conducted. In conclusion, three possible orientation orders were discussed. In these polymers, did you take your measurements in the three directions or did you destroy the orientation before you took the measurements?

M. A. Sahto. There are three orientation orders. It was not our aim to study these effects. We tried to evaluate the properties of relaxed, annealed samples. We observed orientation only in the X-Y direction.

L. A. Utracki. All the samples were annealed under the same condition. The annealing conditions were determined as giving the minimum birefringence value in the X-Y direction for PET without causing any measurable increase in crystallinity.

Some Aspects of the Miscibility Behavior of Polyester/Halogenated Polymer Blends

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Glass transition temperature and depression in melting point methods are commonly used to determine the miscibility behavior of polymer/polymer blends, where at least one component of the mixture is semicrystalline. However, these methods often lead to ambiguous and even contradictory results, as can be shown by several examples. Furthermore, a comparison of the miscibility behavior of poly(vinyl chloride), poly(vinyl bromide), and poly(vinyl fluoride) with linear and branched polyesters indicates that small changes in the structure of the halogenated polymer and/or of the polyester lead to major changes in miscibility, indicating the subtle nature of the miscibility phenomenon and emphasizing difficulties in its control.

INTRODUCTION

The miscibility of polymer/polymer blends can be detected by several methods which have been described in two recent books (1, 2). In practice, two methods are most commonly used for that purpose: the determination of the glass transition temperature, T_g , and the observation of a depression in melting point, T_m . The former measurement can be accomplished by a wide variety of techniques: calorimetry, dynamic mechanical analysis and spectroscopy, to mention just a few. The latter is limited to blends having a semicrystalline component.

A review of the literature, however, indicates that these two accepted methods do not always give consistent answers. It is the first objective of this article to discuss their limitations, using appropriate examples. It is the second objective of this paper to compare the miscibility behavior of poly(vinyl chloride), poly(vinyl bromide), and poly(vinyl fluoride) blended with linear and branched polyesters.

EXPERIMENTAL

All data reported in this article deals with polyester/halogenated polymer blends. More specifically, the following polymer are used:

- PCL: poly(caprolactone)
- PVL: poly(valerolactone)
- PMPPL: poly(α -methyl- α -n-propyl- β -propiolactone)
- PMEPL: poly(α -methyl- α -ethyl- β -propiolactone)
- PBA: poly(butylene adipate)
- PHMS: poly(hexamethylene sebacate)
- PEA: poly(ethylene adipate)
- PVC: poly(vinyl chloride)

- PVB: poly(vinyl bromide)
- PVF: poly(vinyl fluoride)
- PECl (48): chlorinated polyethylene (48 wt. % chlorine)
- PVCl₂: poly(vinylidene chloride)
- PVF₂: poly(vinylidene fluoride)
- CPVC: chlorinated PVC
- PSC: poly(chlorostyrene)
- PSB: poly(bromostyrene)

In this article, the following terminology is retained (T_g method): a blend is declared miscible if it gives a single T_g , intermediate between those of its pure components at all compositions, even if crystals of components 1 and/or 2 are formed. A blend exhibiting two T_g s at a given composition is declared immiscible. According to this terminology, it suffices to observe two T_g s at one composition to conclude that a blend is immiscible, even if the possibility of observing a single T_g at other compositions is not excluded. According to the melting point depression method, a blend is declared miscible if it gives a decrease of T_m with composition and a negative value of the thermodynamic interaction parameter, χ , and immiscible if a constant T_m is observed.

RESULTS AND DISCUSSION

Determination of Miscibility

As mentioned above, miscible polymer/polymer blends exhibit a single T_g at each composition. Two examples of this kind are given in Fig. 1. For PCL/CPVC blends, the T_g -composition relationship is linear and, for PCL/PVB blends, it is concave. These differences in T_g -composition curves for miscible blends are reminiscent of those that are found in random copolymers (5,

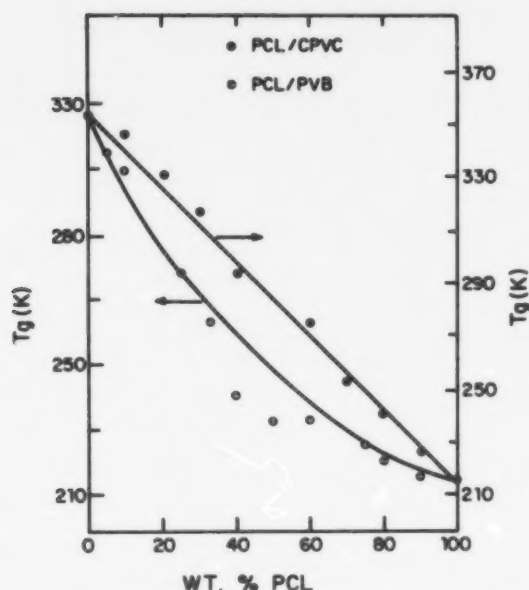


Fig. 1. Glass transition temperature-composition diagrams of PCL/CPVC (3) and PCL/PVB (4) blends.

6). They can be expressed by the Gordon-Taylor equation, which reads:

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \quad (1)$$

where T_g is the glass transition temperature of the blend, T_{g1} and T_{g2} , those of components 1 and 2, w_1 and w_2 , the corresponding weight fractions, and where k is defined by:

$$k = \frac{\alpha_{l2} - \alpha_{g2}}{\alpha_{l1} - \alpha_{g1}} \quad (2)$$

where the α s are the volume expansion coefficients, in the glassy (g) and in the liquid (l) states, of components 1 and 2. Experimentally, k can be determined by fitting Eq 1 to the data shown in Fig. 1. A linear relationship is found if $k = 1$ and concavity when $k < 1$. Equation 1 was derived assuming ideal volume mixing of the two components in the copolymer (and in the blend) and the constancy as a function of composition of the four α s. For PCL/CPVC blends, $k = 1$ and, for PCL/PVB blends, $k = 0.5$. These examples represent extreme cases and, for polymer/polymer blends, k is usually intermediate between these two values. It has been proposed that variations of k are related to changes in the degree of miscibility between two polymers (7).

As mentioned above, blends exhibiting a single T_g are expected to show a decrease of T_m as a function of composition for their semicrystalline component. Literature values indicate that this is usually true. Two examples of this sort are given in Table 1. Similarly, blends exhibiting two T_g s are expected to show a constant value of T_m as a function of composition, and this is generally true. One such example is given in Table 1. However, Table 1 also gives four examples where the T_g and the melting point depression methods disagree. There is

Table 1. Comparison Between the T_g and the T_m Methods to Assess the Miscibility of Polymer/Polymer Blends

Blend	T_g method	T_m method	Reference
PMPL/PVC	Miscible	Miscible	8
PCL/PECl(48)	Miscible	Miscible	9
PMPL/PVF ₂	Immiscible	Immiscible	10
PVL/PVC	Miscible	Immiscible	10
PVL/PVF	Immiscible	Miscible	10
PCL/PVCl ₂	Miscible	Uncertain*	11
PCL/CPVC	Miscible	Uncertain**	3

*Large depression of T_m of PVCl₂ but small decrease of T_m of PCL.

**Depression of T_m of solution-cast blends but constant value of T_m of melt-crystallized blends.

one example where a single T_g is observed without any decrease of T_m , and another example where a decrease of T_m is observed for a blend exhibiting two T_g s.

It is important to realize that several factors can contribute to obtain a melting point depression in polymer/polymer blends:

- Lamellar thickness is not necessarily constant as a function of composition. Khambatta, *et al.* (12), have shown that the crystallite size of PCL in miscible PCL/PVC blends increases slightly with increasing PVC content. This factor should contribute to an increase of T_m as a function of composition; in other words, it reduces the thermodynamic interaction parameter, χ , which is usually calculated from such data.
- Runt, *et al.* (13, 14), have shown that isotactic poly(styrene) (PS) single crystals exhibit a small decrease of T_m when embedded in immiscible matrices such as poly(methyl methacrylate) and poly(butadiene); however, PS single crystals show larger T_m depressions if embedded in miscible matrices. The environment of the crystals then contributes to the calculation of an underestimated χ value.
- Several authors have also reported variations of χ with composition in polymer/polymer blends using small-angle x-ray scattering (15) and inverse gas chromatography (16, 17). These variations were expected since they are usually found in low-molecular-weight mixtures. The PCL/PVCl₂ example of Table 1 can be interpreted on that basis (11): a low value of χ for PVCl₂-rich blends and a close-to-zero value of χ for PCL-rich blends.

Another problem met in the interpretation of melting point depression data lies in the choice of proper crystallization conditions. An illustrative example is shown in Fig. 2 for PCL/CPVC blends (3). Solution cast samples exhibit a melting temperature that decreases with CPVC content. However, melt-crystallized samples show a constant value of T_m , which is increased by annealing and which eventually reaches the value found for solution cast samples. The annealing process is, however, composition-dependent: it is rapid for blends containing small amounts of CPVC, and it slows down with increasing CPVC concentrations. CPVC then acts as a macromolecular diluent. It increases the viscosity of the blend and slows down the annealing process. Figure 2 suggests that the solution-cast

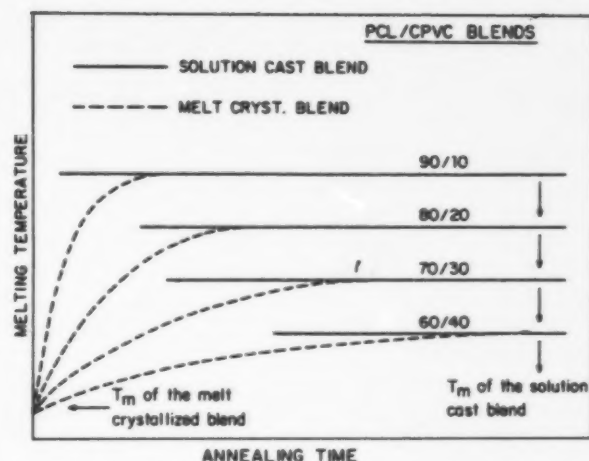


Fig. 2. Schematic diagram of the melting temperature increase as a function of annealing time of PCL/CPVC blends at different compositions.

samples are closer to equilibrium conditions than the melt-crystallized samples and that the former should be used to estimate χ and the miscibility of PCL/CPVC blends.

In view of the preceding remarks, the melting-point depression method presently appears more difficult to interpret and more controversial than the T_g method. For these reasons, the latter is often preferred. In addition, the T_g method is experimentally more accurate and less time-consuming than the former.

Polyester/Halogenated Polymer Blends

Several groups of workers have contributed to show that several linear and branched polyesters are miscible with PVC. Our own group has shown that PVF is immiscible with all available polyesters (10) and that an intermediate situation is found in polyester/PVB blends (4). The available results are summarized in Table 2. It is seen that all polyesters that are miscible with PVB are also miscible with PVC. However, several polyesters are miscible with PVC but not with PVB.

This difference in miscibility behavior upon substitution of the chlorine atom by the bromine atom is seen in other blends. As shown in Table 3, this behavior is also found by substituting PSC by PSB.

Differences in miscibility behavior of PVC and PVF can be understood, since most properties of the chlorine and fluorine atoms are drastically different (Table 4): different ionic and covalent radii, different

Table 2. Comparison of the Miscibility Behavior of Several Polyesters with PVC, PVB, and PVF

Polyester	Polyester/PVC	Polyester/PVB	Polyester/PVF
PCL	Miscible	Miscible	Immiscible
PBA	Miscible	Miscible	Immiscible
PVL	Miscible	Miscible	Immiscible
PHMS	Miscible	Miscible	Immiscible
PMPPL	Miscible	Immiscible	Immiscible
PMEPL	Miscible	Immiscible	Immiscible
PEA	Immiscible	Immiscible	Immiscible

Table 3. Comparison of the Miscibility Behavior of Several Polyesters with PSC and PSB

Polyester	Polyester/PSC	Polyester/PSB
PCL	Miscible	Immiscible
PVL	Immiscible	Immiscible
PHMS	Immiscible	Immiscible
PMPPL	Immiscible	Immiscible

Table 4. Comparative Properties of F, Cl, and Br

Property	F	Cl	Br
Ionic radius (nm)	0.136	0.181	0.196
Covalent radius (nm)	0.072	0.100	0.114
Electronegativity (Pauling's Scale)	4.0	3.0	2.8
First Ionization Potential (eV)	17.418	13.01	11.84
Dissociation Energy (kJ)	158	243	223
Binding energy of the C-X bond (kJ/mole)	485	339	284
Polarizability (cc/atom) $\cdot 10^{24}$	1.04	3.66	4.77

electronegativities, different binding energies of the C-X bond, and different polarizabilities. In fact, differences between fluorine and chlorine atoms are generally greater than differences between the succeeding, heavier halogens. Moreover, fluorinated covalent compounds form a hydrogen bond more easily than other halogenated compounds. It was expected that this tendency would result in better interactions between PVF and polyesters than between PVC and polyesters. However, it seems that PVF forms intramolecular bonds instead of intermolecular bonds, and this leads to immiscible blends with polyesters.

Differences in miscibility behavior of PVC and PVB are more difficult to explain, since all properties of chlorine and bromine atoms are very similar (Table 4). In fact, chlorine and bromine are the most similar of halogens. For example, their small difference in electronegativity suggests that there should be little difference in the degree of covalency of the bonds that they form with any particular element. The experimental results mentioned above are then difficult to understand. They certainly suggest that the miscibility phenomenon between two polymers is due to a delicate balance of forces that is difficult to characterize. Very small differences in properties, as those existing between chlorine and bromine, are sufficient to cross the boundary between the miscibility and immiscibility zones, for reasons that are not clear at the present time.

ACKNOWLEDGMENTS

The author thanks the National Sciences and Engineering Research Council of Canada and the Ministry of Education of the Province of Quebec (FCAC program) for the research grants that supported this work.

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Discussion—R. E. Prud'homme

L. E. St-Pierre. It seems to me that one other number would be nice to have on your last figure—the heat of fusion of these polymers. The thing that impresses me is that something like the fluorine polymer is going to pack very well. It probably has a high heat of fusion and a low rotor energy, at least lower than the bromo. Therefore, I would think that, as it is coming to form the crystal, where it is going after the deepest potential energy well, its ability to exclude any diluent is going to be very good—even a diluent with which it is compatible (say, a diluent that had about equal cohesive energy density). There are two effects: one, a deep potential energy well for the heat of fusion, second, a small rotor energy. Therefore, even at modest temperatures, you would have the ability to obtain the perfect crystal. You cannot get it (i.e., for isotactic polystyrene) because of the high rotor energy. Really, you are not necessarily looking at compatibility, but at the ability of the molecules to form a perfect crystal and, therefore, even to exclude something that is compatible.

R. E. Prud'homme. On the last figures, I did not make reference to the use of the depression in melting-point method. If one considers polyesters blended with PVF or PVC, in these mixtures, only the polyester is semicrystalline. We have not used isotactic materials. For PVF and PVC, I don't really see how the heat of fusion can influence the sort of measurements that we have made, taking into account that PVF and PVC are only in the amorphous phase and never crystallize. What may be important is the glass transition of PVC as compared to that of PVF; but, surprisingly, they are almost similar.

L. E. St-Pierre. To lower the melting point, you have to have some of the other "glop" in the crystal. To come

back to the rotor energy—if the structure is such that you can form crystals easily and thereby exclude the impurities, even in the form of something that is fairly compatible, then you are able to form the crystal. If you cannot do that, then you are going to include these impurities in the crystal. I am not sure that it is a measure of compatibility if it does lower the T_m . Certainly it is in there, but if it does not, it could be compatible, but the crystal is excluding it beautifully and you are forming very nice crystallites.

R. E. Prud'homme. I would also like to remind the audience that PVF₂ is miscible with PMMA. This system is not that different from the system that we have studied. After all, there are carbonyl groups in PMMA, as in polyesters, and between PVF and PVF₂ there is not that much difference. However, miscibility is found between PVF₂ and PMMA but not between PVF and polyesters. Again, this points to the fact that we do not truly understand what is responsible for miscibility. I hope that the coming NMR and FTIR measurements will add to our knowledge in that field.

H. P. Schreiber. I have a feeling of discomfort when one uses what essentially is a thermodynamic parameter, like melting temperature or T_g , as a foolproof index of miscibility. It harks back to some comments made earlier today that the thermomechanical history of the sample at the instant of the measurement can play a dominant role. In other words, as you showed in your slides, the T_m depends critically on whether you cast a solution or melt-crystallize. Is it not possible that T_g could vary critically, depending on how the blends were made? I come to my point. It seems that it would be useful to accept as a criterion on miscibility the *invariance* of a T_g determination. Make your blends, measure T_g , let the blends sit for a long period of time, give them a long temperature condition, and repeat the T_g measurements. If the T_g or T_m remain constant, then this is a reasonable index of equilibrium. But if it starts drifting then, presumably by diffusion mechanism, the material is falling apart, and the miscibility was more artifact of preparation than a thermodynamic fact.

R. E. Prud'homme. You now mention a problem that always exists when dealing with polymers, since it is very difficult to reach equilibrium conditions; in some cases, it may even be impossible. This problem is certainly present when dealing with polymer blends and, to surmount it, blends must be prepared under different conditions. Normally, we prepare blends from solutions, sometimes from two or three different solvents, and also from the melt at different temperatures. Then, we heat-treat the samples at different temperatures. If, after these various treatments, we find the same T_g , we must then be close to equilibrium conditions, but this still does not exclude the possibility of observing artifacts. Sometimes, kinetic processes in polymers are very slow and, if we waited for 20 years, there might eventually be phase separation. There are, however, certain methods that one can use in order to reduce this problem as much as possible. You are right to say that it would be very dangerous to use only one method of preparation or to make blends at only one

composition and to conclude that the blends are miscible. Before talking about miscible blends, I like to make T_g measurements at different compositions. In my jargon, miscibility means that a single T_g can be found at any composition. Of course, we could define miscibility within a narrow range of composition. However, if we can detect miscibility at any composition, then we are putting all chances on our side.

L. A. Utracki. Quite a bit of this discussion is a repetition of the one that we had last year. You can read it in *Polym. Eng. & Sci.*, **22**, 2.

G. Bhatt. You mentioned X-ray diffraction work on blends. Can you elaborate on that? Did you find anything significant?

R. E. Prud'homme. X-ray diffraction experiments on polymer blends indicate that the structure of the semicrystalline polymer is exactly in the same state as it is in the unblended polymer. This observation is also true for blends of PCL with PVC_{12} . A composite X-ray diffraction pattern is then seen: a superposition of those found for the two separate polymers. We did not, however, look at details: we never measured the width of the X-ray diffraction lines. Maybe differences can be found at this level. However, there is no significant difference in the crystalline structure of blended polymers.

G. Bhatt. If there is no change in the crystal lattice parameters, that means that the melt temperature should not change that much. When you have a certain type of crystal, then it should have a particular melting temperature of the pure polymer.

R. E. Prud'homme. The degree of crystallinity of the semicrystalline polymer and its crystal perfection change with blend composition. For instance, DSC measurements indicate a high degree of crystallinity for pure PCL. On dilution with PVC, this crystallinity is initially nearly constant per gram of PCL in the mixture. Above a certain concentration, it falls down rapidly, and then, for the remaining compositions, the system is completely amorphous. Therefore, the blend composition influences the crystallization of the blend and the crystallite size. There is also a depression in melting point.

G. Bhatt. You are relating the crystallite size to a depression of the melting point. An increase in the crystallite size will lead to a broadening of the melting peak but, as far as the peak position is concerned, no matter what crystallite size you have, it will stay the same.

R. E. Prud'homme. In a blend, the depression in melting point is due to the imperfections incorporated into the polymer crystals, and at the same time, the broadening is due to a larger distribution of crystallite size. Both effects are detected simultaneously.

R. S. Porter. There are cases for miscible polyesters where the freezing point or melting point is not significantly lowered on mixing the two together. This is considered as due to minimal entropy of mixing because of the high molecular weights involved. Second point: PVC is exhibiting compatibility with more different polymers than any other polymer. It is interesting that, with polyesters, it seems to be particularly compatible. Is it compatible with poly(butylene terephthalate), which is a mixed aliphatic/aromatic polyester?

R. E. Prud'homme. That is an interesting point. I mentioned that PVC is not miscible with linear polyesters, which have a small number of methylene groups. For instance, a polyester like $(\text{CH}_2-\text{CH}_2-\text{COO})$ is not miscible with PVC but $\{(\text{CH}_2)_4-\text{COO}\}$ is. Similarly for poly(ethylene terephthalate) and poly(butylene terephthalate). The first is not miscible with PVC but the second is.

R. S. Porter. Would you briefly restate your thinking about the hydrogen bonding effects that lead to this compatibility for the aliphatics? Was this your argument?

R. E. Prud'homme. I believe that the main factor leading to miscibility or immiscibility in these two cases is an effect of conformation. In general, miscibility is a result of the presence of hydrogen bonding, dipole/dipole interactions, or a mixture of different interactions. It does not suffice to have a large number of carbonyl groups or a large number of hydrogens available. The polymers have to be in such a conformation that they can match one with the other. I believe that, for the polyesters with a short CH_2 sequence, their conformation is not appropriate to give the necessary interaction.

Recent Advances in Interpenetrating Polymer Networks

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We review the synthesis, morphology, and physical and mechanical properties of IPNs as well as the related pseudo-IPNs, in which only one of the polymers is crosslinked. Recent studies have shown that the degree of phase separation achieved in these materials is strongly dependent on the compatibility of blends of the linear polymer constituents of the IPN components as well as the kinetics of chain extension and the presence of grafting between component polymers. We illustrate this by a series of IPNs consisting of a polyurethane and an acrylic copolymer. The acrylic is a typical automotive enamel. An enhancement in properties results, which is dependent on the amount of grafting and the kinetics of polymerization. Also discussed are IPNs of a polyurethane and an epoxy, which exhibit a synergism in adhesive properties, and IPNs of a RIM polyurethane with several epoxies and unsaturated polyesters. In addition, also reported are the preliminary studies on the first successful preparation of a three-component IPN, consisting of a polyurethane, an epoxy, and an acrylic.

INTRODUCTION

Interpenetrating polymer networks (1-5) (IPNs) are a novel type of polymer alloy consisting of two (or more) crosslinked polymers. They are more-or-less intimate mixtures of two or more distinct, crosslinked polymer networks held together by permanent entanglements with only accidental covalent bonds between the polymers; i.e., they are polymeric "catenanes" (5-7). The entanglements in IPNs must be of a permanent nature and are made so by homocrosslinking of the two polymers. They are produced either by swelling a crosslinked polymer with monomer and the crosslinking agent of another polymer, and curing the swollen polymer *in situ* (2, 4, 8), or by mixing the linear polymer, prepolymers, or monomers in some liquid form (latex (3, 9, 10), solution (11), or bulk (12, 13)), together with crosslinking agents, evaporating the vehicle (if any), and curing the component polymers simultaneously.

IPNs possess several interesting characteristics in comparison to normal polyblends. Formation of IPNs is the only way of intimately combining crosslinked polymers, the resulting mixture exhibiting (at worst) only limited phase separation. Normal blending or mixing of polymers results in a multiphase morphology due to the

well-known thermodynamic incompatibility of polymers. However, if mixing is accomplished simultaneously with crosslinking, phase separation may be kinetically controlled by permanent interlocking of entangled chains.

IPNs synthesized to date exhibit varying degrees of phase separation, dependent principally on the compatibility of the polymers. With highly incompatible polymers, the thermodynamic forces leading to phase separation are so powerful that it occurs substantially before the kinetic ramifications can prevent it. In these cases, only small gains in phase mixing occur. In cases where the polymers are more compatible, phase separation can be almost completely circumvented. Complete compatibility is not necessary to achieve complete phase mixing, since the permanent entanglements (catenation) can effectively prevent phase separation. With intermediate situations of compatibility, intermediate and complex phase behavior results. Thus, IPNs with dispersed phase domains ranging from a few micrometers (incompatible) to a few tens of nanometers (intermediate) (4) and, finally, to those with no resolvable domain structure (complete mixing) (11) have been reported.

IPNs represent a special example of topological isom-

erism in macromolecules; i.e., different ways of embedding these molecules in three-dimensional space. Some permanent entanglements between the different crosslinked networks are inevitable in any sufficiently intimate mixture of the crosslinked networks. These represent examples of catenation in polymer systems. Permanent entanglements are hindering constraints on the motion of segments and ought to simulate covalently bound chemical crosslinks (15, 16).

The combining of varied chemical types of polymeric networks in different compositions, often resulting in controlled, different morphologies, has produced IPNs with synergistic behavior. For example, if one polymer is glassy and the other is elastomeric at room temperature, one obtains either a reinforced rubber or a high-impact plastic, depending upon which phase is continuous (11). In the case of more complete phase mixing, enhancement in mechanical properties is due to the increased physical crosslink density achieved by this interpenetration. Synergistic properties seen in tensile strength (3, 9, 11, 17) and impact strength (11) reflect IPN's special architecture. However, in heterogeneous IPNs, which is the case encountered in most of the studies to date, the effects of interpenetration on the morphologies and the mechanical properties of IPNs have not been clearly identified due to the many factors involved, such as compatibility, intermolecular forces, and grafting.

In pseudo-interpenetrating polymer networks (PDIPN) composed of two chemically different polymers, one is crosslinked and the other is linear. Two different PDIPNs can be distinguished, depending upon which polymer is linear. PDIPNs can be synthesized without the crosslinking agents of the linear component either sequentially or simultaneously, in the same way as IPNs are made. These materials, as well as blends of both linear polymers, should not be capable of limiting phase separation to the same extent as the full IPNs (with both catenated polymers crosslinked), since no topological constraints (i.e., permanent entanglements) exist. In both PDIPNs and linear blends, the linear chains can "disentangle" themselves and phase-separate without breaking covalent bonds. Investigations of these materials along with the full IPNs provide valuable comparative insights on the effect of the permanent, topological entanglements on physical properties (e.g., mechanical properties) and the morphologies of IPNs, as well as, in their own right, providing information about potentially useful polymer composites.

POLYURETHANE-ACRYLIC COPOLYMER IPNS, PDIPNS, AND LINEAR BLENDS

The synthesis of these materials involves, first, the preparation of a) the polyurethane (PU) prepolymer (NCO/OH = 2:1) by reacting one equivalent of poly(1,4-oxybutylene) glycol (M.W. = 1017) with two equivalents of 4,4'-methylene bis(cyclohexyl isocyanate), and b) the acrylate copolymer (AC) prepolymer, composed of eight parts n-butyl methacrylate, one part ethyl methacrylate, and one part styrene. We refer our readers to Ref. 18 for experimental details.

Linear blends were prepared as follows: The PU prepolymer and 1,4-butanediol were mixed thoroughly with the acrylate copolymer syrup. 0.2 percent T-12, dibutyltin dilaurate (by weight of PU) and 1 percent benzoyl peroxide (by weight of AC) were used as catalyst and initiator, respectively. The mixture was cast between two glass plates provided with rubber seals around the edges and subsequently polymerized at 110°C for 24 h. Combinations composed of 20, 40, 60, and 80 percent PU by weight were made.

Two types of pseudo-IPNs were prepared, one from a linear PU/crosslinked AC (PDIPN-2) and the other from a linear AC/crosslinked PU (PDIPN-1). The former PDIPNs were prepared from the mixture of the linear polyurethane component (PU prepolymer + 1,4-butanediol) and the acrylate copolymer syrup with ethylene glycol dimethacrylate (EGDMA). The molecular weight between crosslink sites ($\bar{M}_c$) was 6500. The mixture of acrylate copolymer syrup and the PU prepolymer admixed with 1,4-butanediol and trimethylolpropane (crosslinking agent) resulted in the latter PDIPN. The curing conditions and compositions were the same as in the linear blends.

Full IPNs (FIPNs) were prepared from the mixture of acrylate copolymer syrup with EGDMA and PU prepolymer with 1,4-butanediol and trimethylolpropane. The curing conditions and compositions were the same as those for the linear blends. The crosslinking densities of both polymers were the same ($\bar{M}_c = 6500$). This IPN was prepared in an effort to determine the effects of grafting between the component polymers on the morphology. In an earlier study (19), IPNs of the same PU and a similar acrylic were prepared. In that case, the acrylic was a typical automotive enamel supplied by Inmont Corp. and used with a butylated melamine via pendant hydroxyls on the acrylic. In this system, there were many opportunities for grafting to occur. Note that there were no pendant hydroxyls on the acrylic prepared above (the polymers were the same in every other way). This IPN exhibited a homogeneous morphology, as evidenced by electron microscopy and the presence of one-glass transition.

The following measurements were carried out:

- **Stress-Strain Properties**—The tensile strengths and elongations at break were measured on an Instron Tensile Tester at room temperature with a crosshead speed of 2 in./min. Specimens were 0.125-in.-wide dumbbells.
- **Glass Transition Temperature**—The glass transition temperatures were measured on a Perkin-Elmer Differential Scanning Calorimeter, DSC-2. Measurements were carried out from -120° to +60°C under helium at a scanning rate of 10°C per min. Specimen sizes were on the order of 20 mg.
- **Hardness**—The hardness of IPNs was measured by means of Shore A and D durometers according to ASTM D 2240-75.
- **Kinetic Measurements**—Three different catalyst concentrations were employed for each polymer; i.e., 0.5, 1, and 2 percent of benzoyl peroxide in

the acrylate copolymer; 0.02, 0.1, and 0.5 percent of T-12 in the polyurethane. One g of each sample was poured into a glass tube (12 cm long, 8 mm diameter). The tubes were subsequently sealed. These sample capsules were heated in an oil bath at 110°C. The samples were taken out at intervals and were quenched in a dry-ice-acetone bath and examined for flowability. The gel time was taken as the time at which the polymerizing mass did not flow at room temperature.

- **Electron Microscopy**—The sample preparation was based on Kato's osmium tetroxide (20) staining technique and a two-step sectioning method. The specimens were exposed to OsO₄ vapor and cut with an LKB ultratome III to get a 0.1 μ m slice. The electron micrographs were taken with an AEI 6B and a Phillips 300 transmitting electron microscope with a magnification of 95,000.
- **Mechanical Spectroscopy**—Dynamic viscoelastic properties were obtained using a Rheovibron Model DDV-11 (manufactured by Tokyo Measuring Instruments Co., Ltd., Tokyo, Japan). The measurements were taken over a temperature range of -90° to 80°C using a frequency of 110 Hz and a heating rate of 2°C/min. Sample dimensions were 0.024 $\times$ 0.6 $\times$ 3.5 cm.
- **Density**—The density was measured at room temperature using a hydrostatic technique. The sample dimensions were 0.125 $\times$ 1.25 $\times$ 2.5 cm.

The morphology, as indicated by the glass transition behavior (Table 1) was heterophase. In all cases, two T_g 's, corresponding to the T_g 's of the component polymers, resulted. However, the T_g 's were shifted inward, indicating some phase mixing (interpenetration), most likely at the phase boundaries. The shifts were greatest with the FIPNs, indicating greatest amount of interpenetration. In the case of the full IPNs, intermediate T_g 's occurred (not shown in the Table) depending on the thermal history of the material (21). This would indicate a third phase; i.e., an interpenetrating region. The PDIPNs and linear blends showed no indication of this intermediate phase. Further studies should clarify this situation.

The electron micrographs of the IPNs, PDIPNs, and linear blends all showed heterogeneous behavior, in agreement with the T_g results. The morphology was expected due to the differing solubility parameters of the two polymers. Considering the inwardly shifted glass

transition temperatures obtained by DSC (Table 1), some phase mixing (interpenetration) resulted in all cases. The phase boundaries of the IPNs and PDIPNs-2 were not well-defined, while the PDIPNs-1 and linear blends showed well-defined boundaries. In all cases, the blends having a crosslinked acrylic component exhibited more interpenetration. A possible explanation would be the ease of diffusion of the growing chains. The diffusion rates of the linear and crosslinked polyurethane do not change rapidly during polymerization because the initial prepolymer viscosity is very high. However, the viscosity of the crosslinked acrylic copolymer increases faster than that of the linear acrylate copolymer. Thus, the crosslinked acrylic copolymer does not have enough time to allow complete phase separation for diffusion. This is consistent with the glass-transition behavior being dependent upon the polymerization rates discussed below. Phase inversion was observed to occur around 50 percent polyurethane in all cases. The domain sizes in IPNs and PDIPNs-2 were about the same and ranged from 10 nm to 50 nm. However, the PDIPN-1 and linear blends showed larger domain sizes (50 to 500 nm), indicating more complete phase separation (i.e., less interpenetration). This demonstrates the importance of topology and kinetics on the morphology and degree of interpenetration of these alloys. Since the IPN prepared with the automotive acrylic was homogeneous, this also points out the effects of grafting on the morphology and properties (property enhancement was greater with the automotive acrylic).

DYNAMIC MECHANICAL PROPERTIES

The dynamic storage modulus, E' , vs. temperature for the IPNs, PDIPNs and linear blends shows that the general modulus response to acrylic concentration and temperature is similar for all the alloys. The modulus of the IPNs, the PDIPNs-1, the PDIPNs-2, and the linear blends decreases systematically with increasing polyurethane concentration. This can be seen in Figs. 1 and 2, which show the modulus vs. acrylic composition for a full and a pseudo-IPN. The largest jump of modulus takes place between 60 and 40 percent PU, indicating the phase inversion. The modulus of the alloys increased in the order of linear blends < PDIPNs-2 < PDIPNs-1 < FIPNs at corresponding concentrations. The high degree of phase mixing did not result in an increase of the modulus of these blends; electron micrographs showed more phase mixing in the case of PDIPNs-2 than PDIPNs-1. The damping factor, $\tan \delta$, vs. temperature for the pseudo and full IPNs showed two peaks corresponding to the T_g 's of the polyurethane and the acrylic copolymer networks. The size of the damping peaks changed systematically with concentration of the alloys; i.e., decreased with the respective component concentration.

The modulus-composition behavior of the polyurethane acrylic copolymer IPNs appears in accord with the expected behavior of two phase systems, composed of perfectly adhering phases and a spherical inclusion ("filler") geometry. The Mooney (22) (GM), Kerner (23) (GK₁, GK₂), and Dickie (24) (GD₁, GD₂) equations for

Table 1. Glass Transition Temperature (°C)

	PU 100%	80	60	40	20	0
	PA 0%	20	40	60	80	100
FIPN	204	214	211	209	210	320.5
	—	306	306	306	312	
PDIPN-1	204	211	212	212	210	318
	—	313	317	—	—	
PDIPN-2	204	211	212	213	212	320.5
	—	313	314	—	—	
Linear	204	212	206	205	206	318
Blend	—	320	319	—	—	

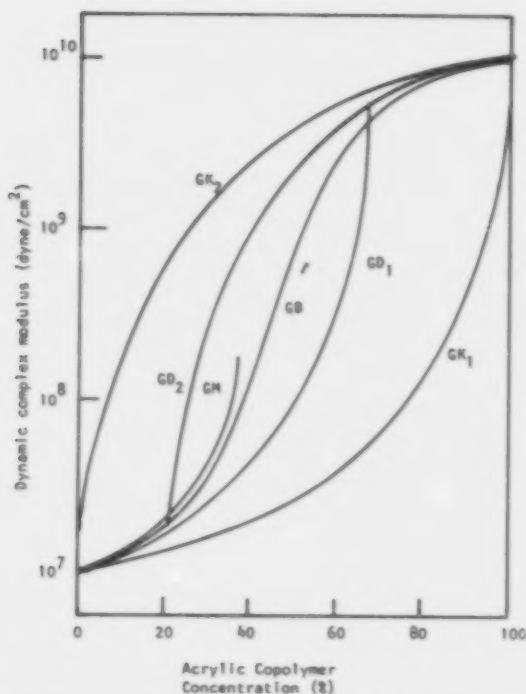


Fig. 1. Dynamic complex modulus vs. acrylic copolymer concentration for PDIPN (X) at 23°C at 110 Hz frequency (solid lines are based on theoretical models).

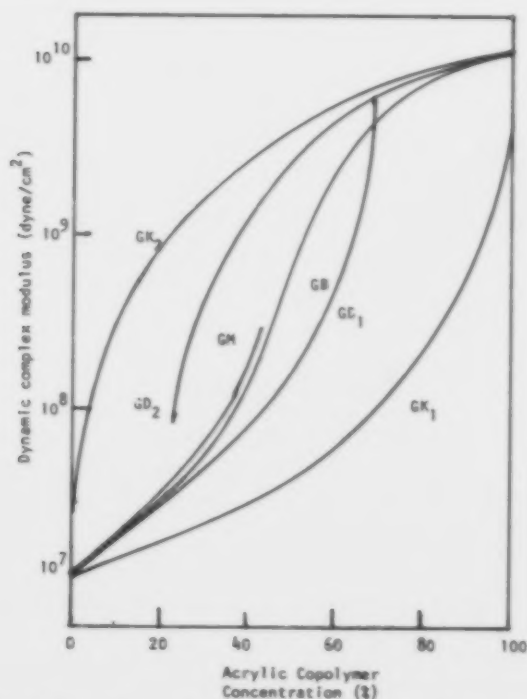


Fig. 2. Dynamic complex modulus vs. acrylic copolymer concentration for FIPN (X) at 23°C at 110 Hz frequency (solid lines are based on theoretical models).

the modulus predicted the modulus fairly well within a narrow range of concentration. However, over the entire concentration range, as can be seen in Figs. 1 and 2,

the experimental values fit the Budiansky equation (25) (GB) best. This was expected, since the Budiansky model can represent the modulus response of a system exhibiting phase inversion. The experimental modulus values of the FIPNs are slightly higher than the Budiansky predictions, while the other materials show lower values than the model, suggesting that a reinforcement effect is achieved only with full IPNs.

The density-composition curve (Fig. 3) shows increased density in all cases, maxima occurring at 80 percent PU. The IPNs exhibited the largest increase at all concentrations. This increase seems to indicate increased molecular mixing in full IPNs. This can be verified by the glass-transition-temperature behavior. Kim, *et al.* (14), explained the increased density of IPNs qualitatively by means of chain entanglements at the domain boundaries. However, it is possible to quantitatively correlate it with T_g shift. As the glass-transition temperatures of the blends shift inward (from T_gA and T_gB to T_gA' and T_gB' , respectively), the volume temperature curves (Fig. 4) of the components in the blends follow the dotted lines instead of the solid lines. Thus, the volume of each component becomes smaller than that of the pure component, which results in higher density at room temperature. Note that the densification of the IPNs is due to interpenetration, which produced the T_g shift, and that the effect was the greatest with full IPNs, in agreement with glass-transition behavior and electron microscopy. Thus, it may be possible to predict the glass-transition behavior of the polymer blends by measuring the densities at several temperatures.

The tensile strengths and breaking elongations of the IPNs as a function of composition are shown in Tables 2

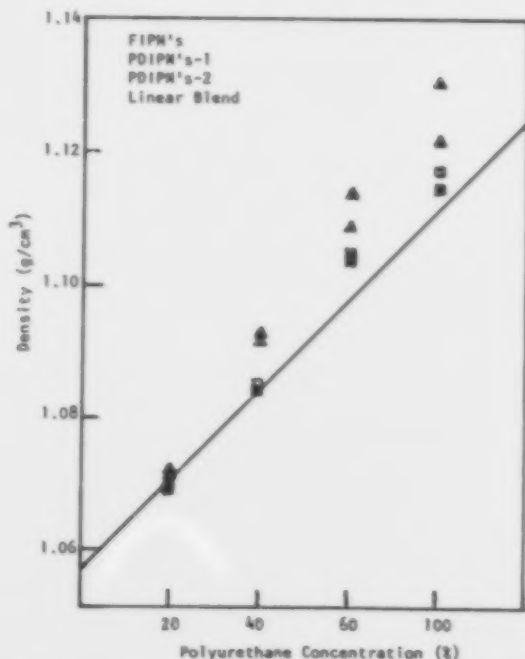


Fig. 3. Density vs. polyurethane concentration for PU-PA (straight line is based on volume additivity).

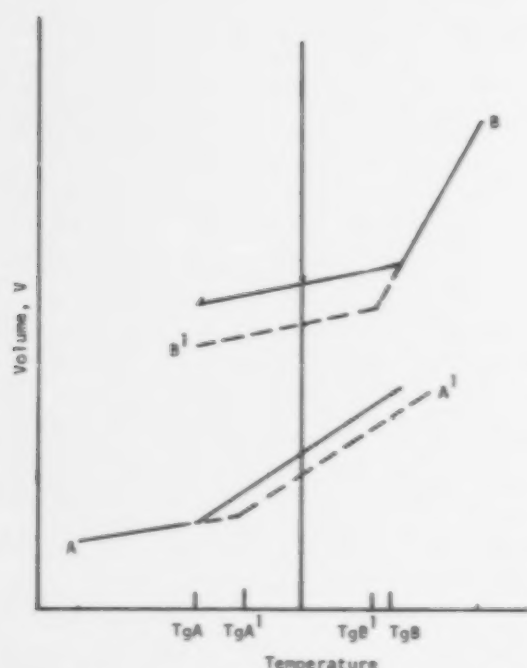


Fig. 4. Volume vs. temperature curves of pure homopolymers and polymer blends.

and 3, respectively. The IPNs show a significant enhancement in tensile strength, particularly at PU/AC = 80:20. The PDIPNs and the linear blends show effectively no enhancement. In all cases measured, the tensile strengths of the IPNs are greater than those of the pseudo-IPNs and the linear blends at the same compositions. In addition, the tensile strengths of both of the pseudo-IPNs are greater than those of the linear blends at the same compositions. The enhancement in tensile strength is most likely due to the higher level of mixing in the IPNs and to greater adhesion between the dispersed and continuous phases. The IPNs should exhibit more complete mixing (less phase separation) and greater phase adhesion due to the permanent entangle-

Table 2. Tensile Strength of IPNs (PSI)

	PU 100%	80	60	40	20	0
	AC 0%	20	40	60	80	100
Full IPN	6100	7100	6525	5000	3715	2571
PDIPN-1	6100	5875	6300	3127	2227	1613
PDIPN-2	5600	4426	5215	3602	3018	2571
Linear Blend	5600	1826	3617	3413	2118	1610

Table 3. Elongation of IPNs (% at Break)

	PU 100%	80	60	40	20	0
	PA 0%	20	40	60	80	100
Full IPN	640	780	540	270	180	15
PDIPN-1	640	540	250	138	120	12
PDIPN-2	610	553	520	276	211	15
Linear Blend	610	640	357	130	195	12

ments (interpenetration) at the phase boundaries.

The elongation, as shown in Table 3, shows a slight increase from 100 to 80 percent PU in the IPNs, indicating the exceptional toughness of this IPN. No increase occurs for the PDIPNs and the blends. A sharp drop in elongation takes place at 60 percent PU, which indicates that a phase inversion occurs around this composition. The Shore A and D hardnesses shown in Table 4 show a rapid increase between 80 and 40 percent PU, which again indicates the phase inversion between 80 and 40 percent PU content.

The gel times of the polymers, shown in Table 5, show the expected trend; i.e., increasing catalyst concentration decreases the gel time. The glass-transition behavior of these IPNs (Table 6) shows that, as the rate of the respective polymerizations increases, the T_g s shift inward, indicating less phase separation. This is most likely due to the fact that increasing the reaction rate lowers the diffusion time allowed for phase separation. The initial prepolymer mixture is single-phase, since the molecular weights are low enough to allow complete mixing. As the polymers are cured, they phase-separate due to their thermodynamic incompatibility. This phase separation is naturally diffusion-

Table 4. Hardness of IPNs (Shore A)

	PU 100%	80	60	40	20	0
	PA 0%	20	40	60	80	100
Full IPN	68 (32)*	70 (35)	80 (38)	92 (53)	94 (63)	100 (72)
PDIPN-1	68 (32)	78 (33)	86 (38)	94 (49)	95 (55)	100 (68)
PDIPN-2	73 (31)	81 (37)	91 (43)	93 (53)	96 (65)	100 (72)
Linear Blend	73 (31)	75 (30)	87 (35)	92 (48)	95 (58)	100 (68)

*Hardnesses in parentheses, are measured by Shore D.

Table 5. Gel Times of Crosslinked Polymers at Different Catalyst Concentrations (min.)

AC	Time	PU	Time
AC-1	4.25	PU-1	12.30
AC-2	4.00	PU-2	7.25
AC-3	3.20	PU-3	3.15
AC-1 (0.5% BPO)		PU-1 (0.02% T-12)	
AC-2 (1% BPO)		PU-2 (0.1% T-12)	
AC-3 (3% BPO)		PU-3 (0.5% T-12)	

Table 6. Glass Transition Temperature of IPNs: Kinetic Results

	AC 40-PU 60 T_g ($^{\circ}$ K)	AC 80-PU 40 T_g ($^{\circ}$ K)
IPN 1.1*	212.2	318.5
IPN 1.2	211	318
IPN 1.3	215	314
IPN 2.1	212	317
IPN 2.2	212.5	316
IPN 2.3	216	313
IPN 3.1	211	314
IPN 3.2	214	308
IPN 3.3	219	293

*IPN 1.1 (IPN from AC-1 and PU-1).

controlled and requires time. If the curing reactions are accelerated, less time will be available for diffusion and subsequent phase separation to occur. When fully crosslinked, further phase separation cannot take place due to topological constraints imposed by the crosslinking of the component polymers. Thus, faster crosslinking would be expected to yield less phase separation. The maximum shift in T_g occurs in the IPN 3 series; in particular, 3-3. In this case, both polymers gel at almost the same time. This is in agreement with the results of Sperling, *et al.* (13), which showed that the smallest domain size of epoxy-acrylic IPNs occurred when the respective curing reactions were closest to simultaneity. The degree of phase mixing, as deduced by the shifts in T_g , are confirmed by the transparency of the IPN films. The transparency increases as the reaction rate increases.

The behavior of this system is quite typical of behavior of IPNs prepared from relatively incompatible polymers.

RIM SYSTEMS FROM IPNS

The spectacular rise of RIM (reaction injection molding) and, more recently, of reinforced RIM (RRIM) in the automotive and other industries has focused attention on relatively high-modulus molded parts, since they can compete successfully with processes such as conventional injection molding and SMC (26, 27). On a volume basis, RIM and RRIM are by far the most energy-efficient materials and processes (12). There are several methods of increasing the modulus of urethane-based RIM parts. They are: increasing the hard segments in the urethane polymer; introducing isocyanurate groups into the urethane polymer (13, 14); and using reinforcing materials (e.g., glass fibers, mica, wollastonite, etc.) in urethane polymers (RRIM).

The disadvantages of RRIM are the relatively high viscosities of the liquid components containing the reinforcing fillers, abrasiveness of the fillers, and mechanical problems with unstable suspensions of solid reinforcements in liquid streams in most currently used RIM machines.

Another method to achieve higher modulus RIM parts is the use of PU-based IPNs in combination with a glassy polymer; e.g., a polyepoxide or unsaturated

polyester. This study describes the use of SIN-IPNs (i.e., simultaneous formation of the polymer networks forming the IPN) consisting of polyurethanes and epoxy or unsaturated polyester. The alloying of the glassy epoxy or unsaturated polyester (relatively high T_g s), respectively, with elastomeric PUs should result in the formation of IPNs exhibiting some properties of reinforced RIMs without the necessity of including solids during the RIM processing (28).

The materials used and their descriptions are listed in Table 7. The polyols and the epoxy resin were demisterized at 80°C under vacuum (1 mm Hg) for about 24 h. The catalysts and the isocyanate were used as received. All the samples were prepared according to the normal processing conditions of RIM technology. The IPNs based on Epon 828 were postcured in an oven at 121°C for 1 h. In the case of the epoxy novolac resin, however, complete polymerization of the RIM plaques required a post-curing time of up to 3 h instead of 1 h at 121°C, although studies are underway to shorten the postcure by the use of higher temperatures.

RESULTS AND DISCUSSION

The formulations, processing conditions, and physical properties of the IPNs, consisting of a combination of urethane elastomers with bisglycidyl ether of bisphenol A (Epon 828), are shown in Tables 8 and 9. (28). The respective reference urethane elastomers are included in these tables for comparison purposes. The catalyst combination of dibutyltin dilaurate (T-12), BF_3 etherate, BCl_3 amine complex, and DMP-30 was selected in order to achieve rapid and complete polymerization of the individual networks. Other effective epoxy hardeners containing active hydrogen atoms were avoided in order to prevent or minimize copolymerization between the epoxy and urethane networks. It is apparent from Tables 8 and 9 and from Fig. 5 that the maximum in tensile strength occurred in IPNs containing 20 percent Epon 828. The flexural modulus increased, while the elongation and split tear tended to decrease with increasing epoxy content. IPNs based on high-modulus urethane elastomer and a combination of epoxy resins (bisglycidyl ether of bisphenol A (Epon 828) and epoxy novolac (D.E.N. 431)) are shown in Table 10. The same trends in physical properties were

Table 7. Materials

Designation	Chemical Composition	Eq. Wt.	Supplier
Niax 31-28	Poly(oxypropylene) triol, ethylene oxide capped and grafted with 21% acrylonitrile	2003	Union Carbide
Niax 50-1180	Mixture of short chain diols	47.6	Union Carbide
Isonate 191	Modified MDI	138.9	The Upjohn Co.
T-12	Dibutyltin dilaurate		M & T Corp.
$\text{BF}_3(\text{C}_2\text{H}_5)_2\text{O}$	Lewis acid-etherate complex		Eastman Chem.
XU 213- BCl_3 (amine) ₂	Lewis acid-amine complex		Ciba-Geigy
DMP-30	2,4,6-Tris(dimethylaminomethyl) phenol		Rohm & Haas
Epon 828	Bis(glycidyl ether) of bisphenol A	185-192*	Shell Chemical Co.
D.E.N. 431	Epoxy novolac resin	172-179*	Dow Chemical
Hysol AC 44368	Mold release agent		Dexter Co.
Glass fibers P 117	1/16-in. milled glass fibers, silane-treated		Owens Corning Fiberglas

*Grams of resin containing one gram-equivalent of epoxide (ASTM D 1855)

Table 8. High-Modulus Urethane-Epoxy IPNs

Ratio Diol/Polyol	30/70	30/70	30/70	30/70	30/70
Niax 31-28	35.3	31.8	28.2	24.7	21.2
Niax 50-1180	15.1	13.6	12.1	10.6	9.1
Isonate 191	49.5	44.5	39.6	34.6	29.7
T-12	0.012	0.012	0.012	0.012	0.012
BF ₃ etherate	—	0.44	0.66	0.66	0.66
BCl ₃ amine complex	—	1.0	2.0	3.0	4.0
DMP-30	—	0.21	0.21	0.21	0.21
Epon 828	—	10	20	30	40
Pot life, s	60	50	60	60	55
Cured in mold, min/°C			← 5/100 →		
Post-cured, min/°C			← 60/121 →		
Shore hardness D	78	85	85	85	85
Tensile strength, MPa at break, 70°F, 21°C	44.8	44.5	49.8	37.5	23.9
Elongation at break, % 70°F, 21°C	30	20	20	10	10
Split tear, KN/m, 70°F, 21°C	61.2	22.0	19.8	brittle	brittle
Flexural modulus, MPa:					
-20°F, -29°C	1920	2238	2543	2738	2746
70°F, 21°C	1007	1311	1593	1815	1702
158°F, 70°C	435	483	580	779	1061
Izod impact, ft. lb/in. ² 70°F, 21°C	6.0	3	5	2.5	2.5
Heat sag, in. (250°F, 121°C, 1 h)	0.5	0.7	0.8	0.5	1.4
Modulus ratio, -29°C/70°C	4.4	4.6	4.4	3.5	2.6

noted as for the above-described IPNs. A maximum in tensile strength was also observed at 20 percent epoxy content (Fig. 5).

Glass-reinforced, high-modulus urethane, RIM elastomers (70/30 polymer polyol/short chain diols) were also prepared for comparison, using silane-treated 1/16-in. milled glass fibers (10 to 30 percent concentration). The resulting properties of the RIM urethanes are shown in Table 11. Comparing Tables 8 and 10, it can be observed that the tensile strength and the other physical properties of the RIM urethane containing 10 percent glass fibers are very similar to the IPN based on 80 percent urethane/20 percent epoxy. The relatively low elongations at break shown in Tables 8 and 10 are due to the high concentrations of hard segments in the urethane network. The elongation can be improved by reducing the content of short diols in the formulation, as can be seen in Table 9. Tables 12 and 13 show the effect of glass-fiber reinforcement on the physical properties of IPNs based on low-modulus urethane

elastomer and 10 or 20 percent Epon 828, respectively. Both combinations exhibit improvement of the tensile strength and heat sag with increasing glass fiber (1/16-in. milled glass fibers) concentration in the range of 10 to 30 percent, as illustrated in Fig. 6. The flexural modulus also increases with increasing glass fiber content, while the elongation and split tear tend to decrease.

The phase relations in the above IPN-RIM systems have been investigated using a Rheovibron and Differential Scanning Calorimeter (28).

TERNARY IPN SYSTEMS

We would like to report preliminary work on the successful preparation of the first three component IPNs using a polyurethane, an acrylic, and an epoxy by means of the simultaneous (SIN) technique.

The polyurethane was prepared by the reaction of a prepolymer consisting of poly(1,4-oxybutylene) glycol of 1000 MW and 4,4'-methylene bis(cyclohexyl

Table 9. Low-Modulus Urethane-Epoxy IPNs

Ratio Diol/Polyol	15/85	15/85	15/85	15/85	15/85
Niax 31-28	55.9	50.3	44.7	39.1	33.5
Niax 50-1180	9.9	8.9	7.9	6.9	5.9
Isonate 191	34.2	30.8	27.9	24.0	20.5
T-12	0.012	0.012	0.012	0.012	0.012
BF ₃ etherate	—	0.44	0.66	0.66	0.66
BCl ₃ amine complex	—	1.0	2.0	3.0	4.0
DMP-30	—	0.21	0.21	0.21	0.21
Epon 828	—	10	20	30	40
Pot life, s	60	60	90	170	240
Cured in mold, min/°C			← 5/100 →		
Post-cured, min/°C			← 60/121 →		
Shore hardness D	68	70	70	73	75
Tensile strength, MPa at break, 70°F, 21°C	24.4	21.8	28.9	25.5	17.8
Elongation at break, % 70°F, 21°C	80	50	30	10	5
Split tear, KN/m, 70°F, 21°C	24.5	22.8	17.5	10.8	brittle
Flexural modulus, MPa:					
-20°F, -29°C	1029	1086	1557	1149	1890
70°F, 21°C	356	362	680	895	920
158°F, 70°C	48	61	118	168	266
Heat sag, in. (250°F, 121°C, 1 h)	1.8	1.7	1.5	1.5	1.5
Modulus ratio, -29°C/70°C	21.3	17.7	13.2	11.1	7.1

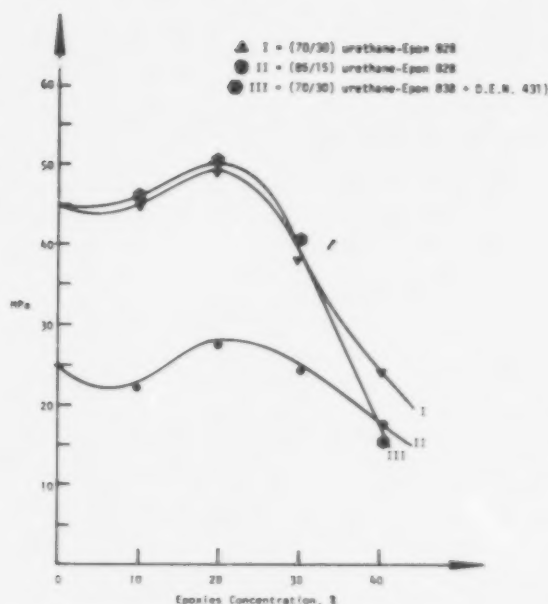


Fig. 5. Tensile strength of IPNs: urethane-epoxies.

isocyanate) (NCO/OH = 2/1) with a 4:1 ratio of butanediol: trimethylolpropane, employing dibutyltin dilaurate as catalyst. The acrylic component was prepared from a prepolymer syrup (15 percent conversion using benzoyl peroxide as initiator) of *n*-butyl methacrylate crosslinked with trimethylolpropane trimethacrylate. The epoxy employed was an epoxy novolac resin (DEN 438, Dow Chemical Co.) cured with a boron trichloride-amine complex (XU-213, Ciba Geigy Chemical Co.).

The preparation of the three component IPNs was accomplished by blending the prepolymers, chain ex-

Table 10. High-Modulus Urethane-Epoxy IPNs (Combination Novolac-Glycidyl Ether of Bisphenol A Epoxies)

Ratio Diol/Polyol	30/70	30/70	30/70	30/70
Niax 31-28	31.8	28.2	24.7	21.2
Niax 50-1180	13.6	12.1	10.6	5.1
Isonate 191	44.5	39.6	34.6	29.7
T-12	0.012	0.012	0.012	0.012
BF ₃ etherate	0.44	0.66	0.66	0.66
BCl ₃ amine complex	1.0	2.0	3.0	4.0
DMP-30	0.21	0.21	0.21	0.21
Epon 828	5	10	15	20
D.E.N. 431	5	10	15	20
Pot life, s	65	90	180	300
Cured in mold, min/°C			← 5/100 →	
Post-cured, min/°C			← 180/121 →	
Shore hardness D	82	83	85	85
Tensile strength, MPa at break, 70°F, 21°C	45.0	51.1	40.2	17.4
Elongation at break, % 70°F, 21°C	15	10	10	5
Split tear, KN/m, 70°F, 21°C	14.7	10.2	brittle	brittle
Flexural modulus, MPa:				
-20°F, -29°C	2223	2459	2666	2678
70°F, 21°C	1378	1661	1877	1778
158°F, 70°C	783	1013	1179	1125
Heat sag, in. (250°F, 121°C, 1 h)	0.8	1.1	1	1
Modulus ratio, -29°C/70°C	2.8	2.3	2.3	2.4

Table 11. Glass-Reinforced Urethane Elastomers

Ratio Diol/Polyol	30/70	30/70	30/70
Niax 31-28	32	28.6	24.9
Niax 50-1180	13.7	12.2	10.6
Isonate 191	44.3	39.4	34.5
T-12	0.010	0.010	0.010
1/16-in. Glass fibers	10	20	30
BCl ₃ amine complex	—	—	—
DMP-30	—	—	—
Epon 828	—	—	—
Pot life, s	50	50	50
Cured in mold, min/°C		← 5/100 →	
Post-cured, min/°C		← 60/100 →	
Shore hardness D	83	85	88
Tensile strength, MPa at break, 70°F, 21°C	50.5	56.4	59.9
Elongation at break, % 70°F, 21°C	15	15	5
Split tear, KN/m, 70°F, 21°C	36	36	26
Flexural modulus, MPa:			
-20°F, -29°C	2461	3376	4382
70°F, 21°C	1610	2159	3067
158°F, 70°C	651	884	1185
Heat sag, in. (250°F, 121°C, 1 h)	0.6	0.5	0.3
Modulus ratio, -29°C/70°C	3.8	3.6	3.7

tenders, crosslinkers, and catalysts (initiator) in varying proportions and degassing the mixtures prior to casting them into stainless-steel molds lined with Mylar film. The IPNs were cured in a platen press at 60°C for 2 h, at 80°C for 2 h, and at 100°C for 12 h at 400 psi pressure. The resulting IPN plaques were uniform in appearance and ranged from translucent to opaque, indicating heterogeneous morphology.

The density and tensile strength of the seven IPNs and the respective pure components are shown in Table 14. The densities of the IPNs, based on hydrostatic measurements (ASTM D-792-66), indicated in all cases higher values than those calculated on the basis of volume additivity of the components. These findings are in agreement with the results obtained on two component polyurethane-acrylics, discussed previously. The same table also clearly indicates significant enhancement of the tensile strength of the IPNs.

Table 12. Glass-Reinforced Urethane-Epoxy IPNs

Ratio Diol/Polyol	15/85	15/85	15/85
Niax 31-28	50.3	50.3	50.3
Niax 50-1180	8.9	8.9	8.9
Isonate 191	30.9	30.9	30.9
T-12	0.012	0.012	0.012
BF ₃ etherate	0.44	0.44	0.44
BCl ₃ amine complex	1.0	1.0	1.0
DMP-30	0.21	0.21	0.21
Epon 828	10	10	10
1/16-in. Glass fibers	10	20	30
Pot life, s	150	180	270
Cured in mold, min/°C		← 5/100 →	
Post-cured, min/°C		← 60/121 →	
Shore hardness D	75	75	75
Tensile strength, MPa at break, 70°F, 21°C	25.1	28.1	30.9
Elongation at break, % 70°F, 21°C	40	20	20
Split tear, KN/m, 70°F, 21°C	25.2	23.6	22.2
Flexural modulus, MPa:			
-20°F, -29°C	1506	1793	2237
70°F, 21°C	600	780	819
158°F, 70°C	129	205	264
Heat sag, in. (250°F, 121°C, 1 h)	1.0	0.8	0.7
Modulus ratio, -29°C/70°C	11.7	8.7	8.5

Table 13. Glass-Reinforced Urethane-Epoxy IPNs

Ratio Dio/Polyol	15/85	15/85	15/85
Niix 31-28	44.7	44.7	44.7
Niix 50-1180	7.9	7.9	7.9
Isonate 191	27.4	27.4	27.4
T-12	0.012	0.012	0.012
BF ₃ etherate	0.66	0.66	0.66
BCl ₃ amine complex	2.0	2.0	2.0
DMP-30	0.21	0.21	0.21
Epon 828	20	20	20
1/16-in. Glass fibers	10	20	50
Pot life, s	120	150	180
Cured in mold, min/°C		← 5/100 →	
Post-cured, min/°C		← 60/100 →	
Shore hardness D	80	80	80
Tensile strength, MPa at break, 70°F, 21°C	30.9	31.5	33.4
Elongation at break, % 70°F, 21°C	10	10	10
Split tear, KN/m, 70°F, 21°C	23.2	21.4	18.4
Flexural modulus, MPa: -20°F, -29°C	1761	1971	2284
70°F, 21°C	965	1004	1005
158°F, 70°C	168	193	349
Heat sag, in. (250°F, 121°C, 1 h)	1.2	1.1	1.0
Modulus ratio, -29°C/70°C	10.5	10.2	6.5

ACKNOWLEDGMENTS

The authors wish to express their appreciation to Dr. H. K. Yoon of Johnson & Johnson; Dr. Roberto Pernice of Montepolimeri, P. Marghera, Italy; and to Mr. Vijay Parakh of the Polymer Institute, University of Detroit, for their contributions to the acrylic IPNs, RIM-IPNs, and ternary IPNs, respectively. The authors also wish to acknowledge the support of the National Science Foundation under Grants No. DMR-780593802 and DAAG2981K0093.

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FIGURE 6. Tensile Strength of Glass-Reinforced IPN's

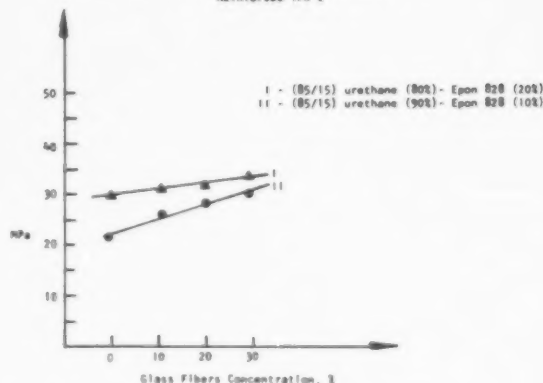


Fig. 6. Tensile strength of glass-reinforced IPNs.

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Table 14. Density and Tensile Strength of Ternary IPNs

Sample No.	PU %	PA %	PE %	*Calculated (g/cc)	Measured (g/cc)	Tensile Strength (psi)
IPN 1	12.5	12.5	75.0	1.182	1.186	5760
IPN 2	12.5	75.0	12.5	1.085	1.095	2660
IPN 3	75.0	12.5	12.5	1.127	1.144	3950
IPN 4	33.3	33.3	33.3	1.131	1.141	3000
IPN 5	50.0	25.0	25.0	1.131	1.139	4610
IPN 6	25.0	50.0	25.0	1.112	1.128	3115
IPN 7	25.0	25.0	50.0	1.152	1.161	5340
8	100				1.124	3800
9		100			1.057	2570
10			100		1.213	3300

*Based on the volume additivity of the components.

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Discussion—K. C. Frisch

L. A. Utracki. I am surprised to hear you saying that the domain size in the IPNs is of the order of 100 Å and, at the same time, that there is a distinct separation of T_g s. This means that T_g must detect domains of at least this order of magnitude. That is quite surprising. We have prepared IPNs without microstructure. In fact, we used PPO/PS from GE.

K. C. Frisch. We slightly brominated the poly(phenylene-oxide) and crosslinked this with ethylene diamine. Then, we crosslinked styrene with divinyl benzene. In other words, we made the full IPN, the semi-IPN, and the linear blend, and got a single glass transition—no fine structure! This was the only case, as far as I know, where you really have a broadening of T_g peaks but single T_g and no fine structure by the electron microscopy. As far as I know, this is really the only *bona fide* case of a miscible blend published.

L. A. Utracki. I think that we should be very grateful for this comment. It indicates the wisdom of thermodynamic definitions. From the thermodynamic point of view, you have only one type of miscibility. There is no sense talking of various miscibilities. Miscibility means one thing and only one thing—miscibility on the molec-

ular level. This means that you have to go down to the Å scale. If you have 50 or 100 Å domains, it means that the system is immiscible.

K. C. Frisch. In connection with thermodynamics, I would like to mention some very interesting work that has been done in the laboratories of Prof. Lipatof at the Macromolecular Institute in Kiev. Along with IPNs, they are working on these things.

R. S. Porter. You find a maximum intermediate between the two limited concentrations; for example, with the urethane and acrylic. What do you envision as a possible mechanism for this maximum?

K. C. Frisch. This would appear to be essentially due to physical crosslinks. Say, due to interpenetration, almost like reinforcing effects. We did, at one time, determine the crosslink density, but by a wrong method (swelling). As an approximation, we did get a maximum approximately where the maximum of tensile strength occurs. However, the reason why I am saying that this is an approximation is that this should be theoretically applicable only to a homopolymer. The swelling characteristic indeed varies. Nevertheless, it was interesting that one gets a swelling at these maxima, presumably due to this interpenetration. The greater the "compatibility," the greater the interpenetration. A smaller particle size will give you the greatest adhesion between the phases.

R. S. Porter. I thought that, from crosslinking density theory, you would calculate less swelling right at the maximum for higher crosslink density.

K. C. Frisch. This is correct. Here, the compression modulus was measured before and after, and indeed, it does go down. Yes, you are absolutely correct.

V. Di Tullio. Going back 20 years ago, when the catenanes were first suggested, there was a big question as to how you prove that you really have a catenane. Is this actually just a surface?

K. C. Frisch. Catenanes have been produced in organic chemistry. They were sort of an academic curiosity. There was even a fake patent out from Germany, which was later found to be incorrect. We carried a partial structure proof. We did this with emulsions; we used urethane/urea emulsion, polyether based, and an acrylic. This was the IPN. You can make IPNs from emulsions or from solutions, 100 percent solids, and we made foams. We cleaved the urethane by means of 10 N HCL. We obtained a film. Since the urethane went into solution, its density was very much lower, but it was still a perfectly intact, but weak, film. Then, separately, we took the same urethane and partially hydrolyzed this with 10 N HCL. The reason why we did it, partially, was because we wanted to show that this was not a pure solubility and noncovalent bond.

Development of Industrial Polyolefin Blends using Melt Rheology Data

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The review of current knowledge of the composition dependence of polymer-blend processability and morphology shows that development of industrial blends requires use of a semiempirical approach, based on the particular rheological composition (PRC) concept. Selecting blend composition in the close proximity to PRC and employing factorial experiments for the mixing process allows the development of successful industrial polyethylene/polypropylene blends designed for film and blow-molding applications.

INTRODUCTION

The primary aim of applied melt rheology of polymer blends is to enhance processability of poly-polymer compositions of unique performance characteristics and to promote understanding of relationships between blend morphology and melt rheology so as to rationalize manufacturing (melt-mixing) processes in blend production. Melt rheology is understood here as a set of numerical approximations of known reliability for viscosity and elasticity functions, which we will endeavor to relate to blend supermolecular structure (morphology) as (indirectly) revealed by the particular compositions, specific melt volume, and stress dependence of recoverable strain.

The title limits the scope of our consideration to the most common polyolefin class of microheterogeneous blends. However, we hope to render generality to our findings by investigating mixtures distinctly different in components' "wettability" (interface layer performance) and macromolecular size (average molecular weight). Both rheogoniometric and capillary rheometry-derived rheological characteristics will be employed so as to estimate instrument effect and to render the characteristics over a broad range of shear (1).

In view of several comprehensive reviews of both "conference proceedings" (2-4) and "rationalized approach" (5-11) type, it would be superfluous to attempt a summary here. It seems appropriate, however, to underscore the fact that engineering applications of research on molten blend rheology have so far been hampered by their limitation to linear viscoelasticity of blends (e.g., blending laws of Ninomiya and of Bogue (12, 13)), as well as by considering only melt viscosity in the Newtonian regime for blends of accidentally selected components. The problem of component and composition dependence of blend-melt rheology ap-

pears to be as difficult as it is important for engineering applications. Some attempts to forward a viable solution to this problem in reference to melt viscosity has been made (14), whereas a comprehensive treatment of melt viscosity and elasticity, successfully approached with H. Van Oene's theory (5a), still requires quantitative experimental evaluation (5b). Approaches to the composition-rheology relationship for polymer blends below melting (softening) temperature in the terms of phenomenological models (e.g., p. 239 in (2)), appear unsuccessful in application to molten blends (15). The empirical (curve-fitting) procedure for tackling melt viscosity-composition dependence of Carley (16) has yet to be extended to melt elasticity and, if proven equally successful, it would require further development toward extending the range of shear to that pertinent for engineering applications and toward an understanding of the physical and structural regularities contrived and implied by this approach.

A brief perusal of review literature (e.g., (5)) reveals that numerous contemporary researches on the polyolefin blends are sophisticated repetitions of work carried out a decade or so ago; e.g., on their structure, relaxation spectra (6, 17-21), performance characteristics (22-24), and melt viscoelasticity (25-28). Granting the profound influence upon our knowledge of polyolefin blends of these contemporary studies, their repetitive character leaves untapped the vast range of binary polyolefin mixtures, consisting of polymers of molecular weight, branching, "wettability," and viscoelasticity ratios substantially different from those investigated so far.

The particular rheological compositions (PRC) are defined for our purpose as the compositions at which maxima and/or minima on the graphs presenting composition dependence of viscosity η^0 , and elasticity ψ_1^0 functions (see Table 1 for definitions), as well as of the derivatives (e.g., flow n and elasticity m exponents) are observed (Fig. 1).

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Table 1. Melt Rheology—Approximations for the Material Functions

Viscosity	General	Elasticity High Shear Estimates
shear stress	elasticity coefficient:	principal normal stress
(1) $p_{12} = p_{12}^0 \cdot \left(\frac{\dot{\gamma}}{\dot{\gamma}^0}\right)^n$	$\psi_1 = \frac{N_1}{\dot{\gamma}^2}$	(2) $N_1 = N_1^0 \left(\frac{\dot{\gamma}}{\dot{\gamma}^0}\right)^m$ $\beta = \left[1 + 0.5 \left(\frac{N_1}{p_{12}}\right)^2\right]^{1/2}$
viscosity function: power law—	relaxation time:	(Tanner [39] recoverable strain:
(3) $\eta = \eta^0 \cdot \dot{\gamma}^{n-1}$	$\tau = \frac{\psi_1}{2\eta}$	$\gamma = \frac{N_1}{2p_{12}} = \sqrt{2(\beta^2 - 1)}$
or log parabola approximations	relaxation time function	$\gamma = \text{const. } p_{12}^b$ [41]: (for $b < 1$, $(1/d) < 40$)
(5) $\ln \eta = A0 + A1 \ln \dot{\gamma} + A2 \ln^2 \dot{\gamma}$	(7) $\ln \tau = C0 + C1 \ln \dot{\gamma} + C2 \ln^2 \dot{\gamma}$	$\gamma = \sqrt{(b^2 + 1)(\beta^2 - 1)}$
standardized viscosity: $\eta^0 = p_{12}^0 $ or e^{A0} , power law (viscosity) exponent $n \sim A1 + 1$.	standardized relaxation time $\tau^0 = e^{C0}$	$\gamma_w = \sqrt{2(\beta^2 - 1)}$ (strain on the capillary wall)
		$F = \frac{\gamma_w}{\gamma} = \sqrt{\frac{3n+1}{2(5n+1)}}$ (Utracki [40])

at standardized shear rate, $\dot{\gamma}^0$ of 1 s^{-1}

PRC follow in a trivial way from the pattern of melt viscosity and elasticity functions when plotted on respective graphs with the blends composition as parameter (29) (Fig. 2). It should be underscored that the occurrence of crossovers of melt viscosity and elasticity functions on such graphs increases with heterogeneity (e.g., *MWD*) and average molecular weight of the components: for low-molecular-weight polyethylene blends, the viscosity curves are parallel and could be shifted for "composition superposition" (37, 38). With increasing $\bar{M}$, *MWD* of components, the crossovers (and, hence, PRCs) are amplified (38).

Although PRCs were reported implicitly in the early '60s for the viscosity function (30) and shortly thereafter

for the elasticity function (31), their significance is still subject to controversy (see footnote in (5b)) and a "forced-fit" linear composition dependence for blends viscosity is pursued (30, 32, 33). Nevertheless, vast experimental evidence due to C. D. Han (9), and theoretical evidence due to H. Van Oene (5a), as well as intuitively obvious dependence of the molten blends morphology (see, e.g., specific volume, Fig. 3) and the interface layer (34-36) upon shear stress and amount of strain (11) seem to substantiate PRCs' importance for the engineering rheology of polymer blends.

Industrial applications of PRC require, therefore, a judicious selection of approximations for the rheological functions: employing their power law or logarithmic

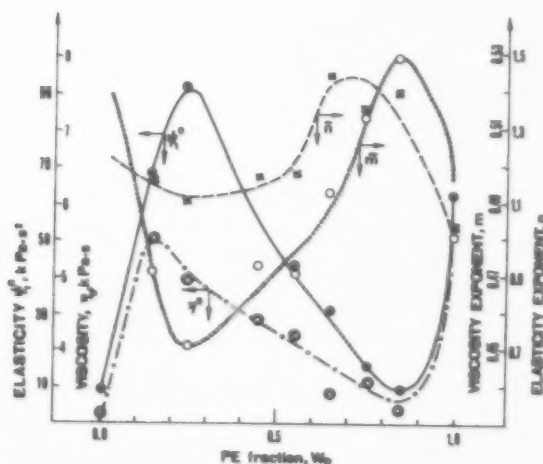


Fig. 1. Composition dependence of viscosity, η^0 , and elasticity, ψ_1 , for i-PP/LDPE blends at 463K. Note particular rheology composition at ~0.2 and ~0.8 wt. fraction of LDPE (Courtesy Academic Press, 1978 (5)).

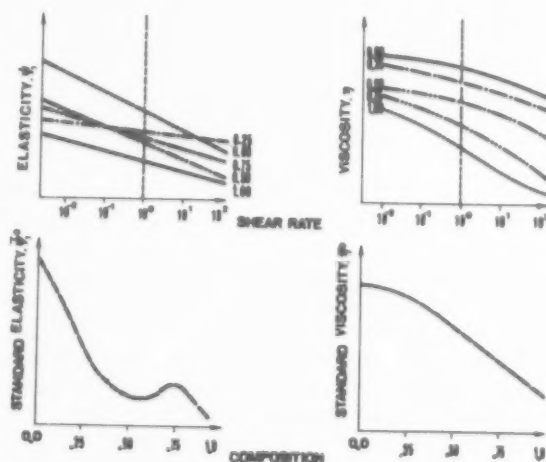


Fig. 2. Formal origin of the particular rheology composition (PRC) for melt elasticity, ψ_1 , and a binary polymer blend. This hypothetical blend does not display PRC with respect to melt viscosity, η .

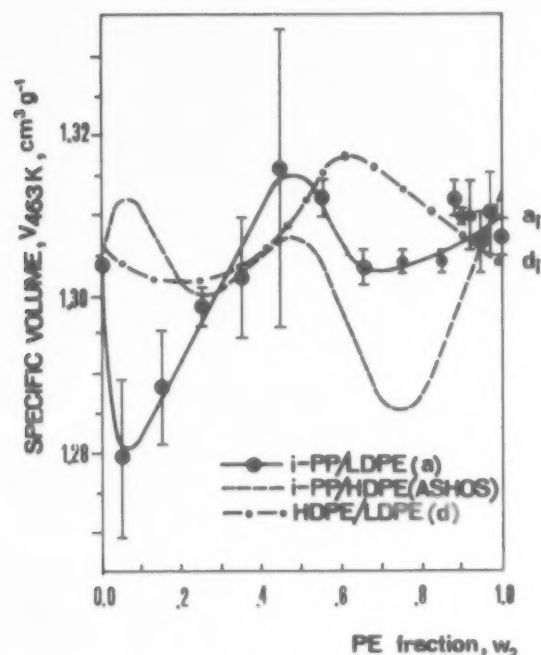


Fig. 3. Composition dependence of the specific melt volume at 463K, v_{463} for i-PP/LDPE (d), i-PP/HDPE (ASHOS), and HDPE/LDPE (d) blends (Courtesy Polimery (Warsaw, 1978).

parabola presentations, one has the opportunity to express the functions, over a comprehensive range of shear rate (or stress) by pairs, of the approximation parameters $\eta^0 - n$, $\psi_1^0 - m$, etc. (Table 1) with specified confidence limits.

Note that the melt viscoelasticity functions employed, not only localize the particular compositions for viscosity, η^0 , elasticity, ψ_1^0 , and their rate derivatives (n and m , respectively), but also render it possible to evaluate η , ψ_1 at any level of shear rate within the range for which functional approximations were established from experimental data.

Development of an Industrial Blend using Particular Compositions (PRC) and "Discrete Composition Sampling" (DCS) Technique

The technique consists of preparing a number of composition sampling blends, carrying out the melt rheology characterization, with data treatment yielding approximation equations with evaluated parameters (Table 1) and, finally, plotting the parameters for DCS blends and components as a function of the composition. A 10 wt. % composition spacing is usually a reasonable minimum for evaluation of a binary polymer system; the melt-mixing technique should obviously be as similar as feasible to the industrial mixing process.

The melt rheology functions for blends and components should be evaluated over the "industrial" range of rate, stress, temperature, etc., variables. It was found convenient to distinguish between the following approximations for melt-rheology functions. "A"-least squares parabola approximation for low (e.g., cone-plate) and high (capillary) viscometer shear data (joint approximation); "B"-approximation for low shear data,

and "C"-approximation over higher shear data. Values of the approximation equations parameters for "A", "B", and "C" will obviously differ, as illustrated with plots for composition dependence of melt elasticity, ψ_1^0 from "A" and "C", compared with the dependence of the "point" elasticity measure in the form of a Melt Memory Index, MMI, in Fig. 4. Although presentation "A" is the most versatile and reliable, approximation "C" is adequate for most technical applications and definitely more accurate in localizing PRC than the technical point measure of melt elasticity—MMI.

The source of data for the melt viscoelasticity consists of cone-plate measurements (approximation "B" for normal stress difference, N_1 , is illustrated with Fig. 5) and capillary rheometry (viscosity and extrudate swelling—see Table 1)—the latter for "C" and "A" approximations. It should be borne in mind that both the selection of viscoelasticity function, especially in the case of elasticity (recoverable strain, γ , elasticity coefficient, ψ_1 , or modulus, G (28)), and of the instruments employed (e.g., constant stress or constant rate capillary rheometer) affect the data and, hence, PRC placement.

Having established the requirement for reliable "A" and "C" presentations of the viscoelasticity of the molten blends, we may proceed with exploitation of the approximation parameters for finding the composition at which the system displays best processability and, hopefully, adequate performance characteristics. Using data for i-PP/LDPE (a), i-PP/HDPE (ASHOS), and HDPE/LDPE (d) blends, characterized in with Tables 2 to 4 (and Ref. 28), we will endeavor to describe the application of the particular composition—"PRC" concept for selecting the composition of an industrial blend. Taking as an example the film grade of an iPP/LDPE blend, one would look for a composition for

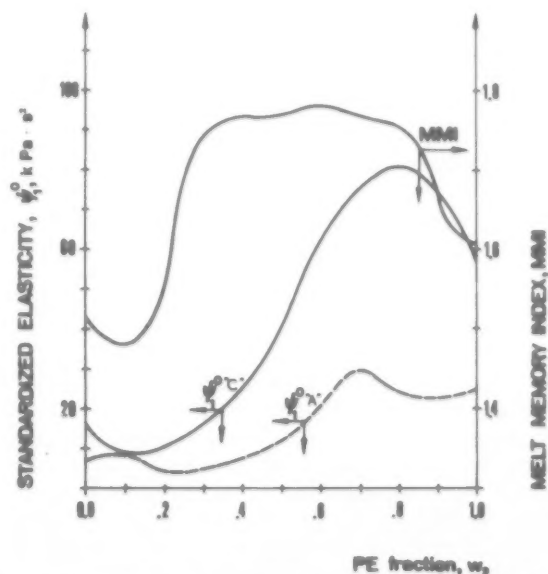


Fig. 4. Comparison of the composition dependency of standardized at $\dot{\gamma}^0 = 1 \text{ s}^{-1}$ melt elasticity, ψ_1^0 (see Table 1), evaluated via "A" and "C" approximations with that for melt memory index (ASTM D1238) 463K, HDPE/LDPE blend.

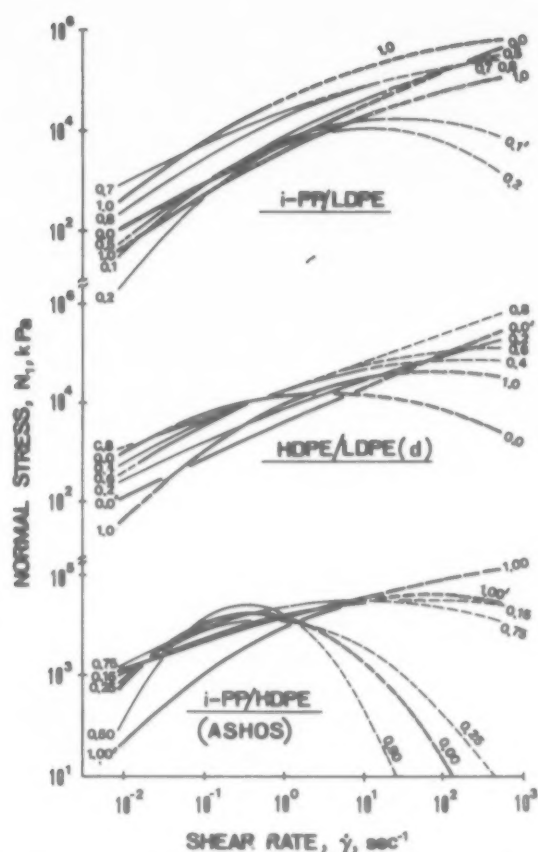


Fig. 5. Shear-rate dependence of normal stress difference, N_1 , for polyolefin blends listed in Fig. 3. Approximation "B," WRG16, 463K.

which melt viscosity, " η^0 ," and its rate dependence (power law exponent), " n ," go through a minimum: indeed, for the system considered, such PRC appears in the vicinity of 80 percent of LDPE, albeit, as evident from Fig. 6, " n " goes through a maximum. Nevertheless, considering the sharpness of the " n " maximum, it seems reasonable to assume that a small shift in composition from the PRC would result in a rapid drop in " n " and, hence, in a substantial increase in the rate dependence of melt viscosity. Considering the low temperature sensitivity of polyethylene melt viscosity, its strong rate dependence is an advantage from the standpoint of manufacturing or processing operation control.

Complementary requirements for good processability of film-grade resin call for a not-too-high melt elasticity (43, 44), whereas (in the case of "viscosity" PRC) a single pair (η^0 , n) of melt characteristics was adequate, in order to evaluate "elasticity" PRC, a coupled pair of rheological characteristics have to be considered: elasticity, ψ_1^0 , and its rate dependence, m (Fig 7), as well as characteristic relaxation time, τ^0 . In Fig. 8, the composition dependence of τ^0 is presented for the "A"-type approximation, hence, also encompassing slow (e.g., the extrusion-blowing film) flow.

Considerations similar to these for "viscosity" PRC lead to the conclusion that the ψ_1^0 maximum at ca. 80 percent LDPE should not be detrimental from the

standpoint of processability because of the "associated" minimum in the exponent of elasticity, m . The film-grade composition might, therefore, be tentatively selected at >80 percent LDPE, its actual value to be ascertained from the performance characteristic for pilot-size experimental batches of the blend.

It is worth underscoring the fact that the significance of relaxation time estimate, τ^0 , lies not only in its capacity as an auxiliary check for "elasticity" PRC. This application of τ^0 follows directly from the relaxation time concept (12, 13, 25, 26). τ^0 is, moreover, a measure of molten blend components' deformability; it can be used in processability scale-up or in extrusion process stability evaluation.

In practical applications, composition selection employing PRC requires a joint plot for viscosity and elasticity functions presented by their approximation parameters—as derived from melt rheology evaluation performed on the composition sampling blends. A working plot, such as presented in Fig. 1 for the iPP/LDPE system, allows for educated guess adjustments in the industrial blend composition, necessitated by performance characteristics of the final product.

Melt Rheology: Applications in Manufacturing Industrial Blends

Reliable and comprehensive melt rheology characteristics for the blends and their components do find more applications in manufacturing and processing than just selection of the composition. Even simple rheo-technical screening with time-dependence of the standard flow rate (ASTM D-1238) is quite effective in the evaluation of rheothermal stability, for both components and the blends.

The test is based on measurements of melt-flow rate for samples held in the plastometer reservoir for times ranging from the standard six min up to 1 h. The samples are either "as received"—marked with "O" on Fig. 9, or those held at 100°C for 24 h prior to the measurement ("24"). The differences among LDPEs, polypropylenes, and their blends (Blenden-PII020/D1—blow molding and Blenden-PII020/F1—film grades) with respect to rheothermal stability are evident. The above-described melt-stability ratio (MSR) test is used or both batch-to-batch uniformity screening of components and for the blends, as well as for evaluating the stability of a blend in processing operations varying in duration.

Melt-rheology characteristics are also useful for designing the melt-mixing process, albeit their semiquantitative exploitation is feasible so far for the evaluation of laminar mixing (e.g., in the single-screw extruder-homogenizer/pelletizer). Since attempts to formulate rheology governing dispersive melt-mixing processes have not been successful, description of the mixing in a Banbury-type mixer involves factorial design experiments (47, 48). With this technique, we seek relationships between operating parameters for mixer (barrel temperature, T_b , ram pressure, p_r , and mixing time, t —represented as the reduced parameters, X_1 , X_2 , and X_3 , respectively) and the blend properties: flow rate (FR), melt elasticity (MMI), as well as density (d_{23}^4) and

Table 2. Characteristics of HDPE"/LDPE" Blends—Type "d"

Characteristic (± standard error)	ASTM method D-	0	20	40	60	80	100	Comments
Density, d_{20}^* , kg/m ³	1595-68 ^{a)}	960.1	953.2	944.6	936.1	928.1	915.5	a) Titration
Specific volume, v_{20}^* , cm ³ /g	— ^{b)}	1.314	1.302	1.305	1.318	1.309	1.354	b) Dtd. in FR measurement
Melt Flow Rate, FR, 2.16KG, 463K	1238-73"E"	0.23-30	0.38-46	0.60-72	1.27-1.50	2.73-3.68	14.9-18.0	c) Extrudate swell in FR measurement
Melt Memory Index, MMI, %	— ^{c)}	129	133-145	139-142	144-146	150-193	86	d) Tetralin, 393K, ml/g
Limiting Viscosity Number, LVN (soln.)	1601-61 ^{d)}	250	179	157	133	108		e) Polarizing microscope
Melting Temperature Interval, ΔT_m , K	2117-64 ^{e)}	408	400-407	403-406	404-407	405-408	381	f) Sample #3, speed C
Tensile (yield) strength, R_e , MPa	638-72 ^{b)}	33.4 ± 3.0	23.8 ± 1.4	17.3 ± 2.5	14.3 ± 1.5	12.1 ± 1.0	9.9 ± 0.1	g) Sample annealed and slowly (5 K/h) cooled [g]
Storage modulus, $G'_{25\pm 0.5}$, MPa	2236 ^{a)}	812	655	490	356	236	153	h) Estd. from LVN
(torsion pendulum)	2240-75	70	67	65	61	55-57	46.4	i) $\eta_w^0 = \rho^0 $ at $\dot{\gamma}^0 = 1 \text{ s}^{-1}$
Hardness, H_{500}	2236	1.22	1.31	1.49	1.86	2.14	3.16	k) MC rheometer, (l/d) = 40.3
Free oscillation damping, $A_{200 \pm 100}$	— ^{b)}	14.0	9.2	7.7	6.3	4.8	3.6	l) "R16" WRG (rheogoniometer)
Average mol. mass, $M_v \cdot 10^{-4}$	2238-68"A"	0 (reference)	3.87	8.87	13.7	17.0	30.0	m) M# : numbers ordering replications
Short chain branching, SCB CH ₃ /1000C	—	125.3 ± 4.8	100.7 ± 5.0	78.6 ± 4.2	47.2 ± 2.5	21.9 ± 1.9	14.8 ± 1.4	n) Supplier: "Rigidex 2" British Petroleum, England
Standardized Melt Rheology Characteristics @463K	1703-62 ^{b)}	508 ± 10	532 ± 13	505 ± 12	552 ± 12	636 ± 20	594 ± 28	
— Viscosity, η^0 , kilopoises	— ^{b)}	2.22 ± 0.23	1.38 ± 0.27	2.35 ± 0.22	1.67 ± 0.12	1.70 ± 0.15	0.59 ± 0.08	
— Viscosity exponent, $n \cdot 10^4$	—	673 ± 26	894 ± 54	764 ± 25	741 ± 19	634 ± 30	726 ± 35	2) "Fortene XX" Montedison S.p.A., Italy
— Elasticity, ψ^0 , 1/dynes · cm ⁻² · s ² (10 ⁴ Pas ²)	—	d 0	d 2	d 4	d 6	d 8	d 10	
— Av. elasticity exponent, $m \cdot 10^3$	— ^{m)}	(Ri) ¹⁾	M10 - 12	M7 - 9	M - 6	M1 - 3	(Fe) ²⁾	Mixing on the roll mills
Designation	—							

Table 3. Characteristics of I-Polypropylene/HDPE Blends—type ASHOS

Characteristic ($\pm$ standard error)	ASTM method D-	0	15	25	50	75	100	Comments
Density, d_4^{20} , kg m $^{-3}$	1505	907	912.7	917.1	926.9	936.4	947.4	a) R. Chiang '58
Specific volume, v_r , cm ^{3} g $^{-1}$	—	1.3217	—	—	—	—	1.3327	b) J. B. Kisinger '59 (see [5] for ref.)
Melt Flow Rate, FR, 463K	1238	8.5	10.6	11.6	13.6	11.5	2.4	c) $[\eta]_{sp}^0 = [\eta]_{sp}^0$ from power law approximation
Limiting Viscosity Number, ^{o}	1601	419	363.9 $\pm$ 22.7	352.1 $\pm$ 11.3	307.3 $\pm$ 7.2	264.3 $\pm$ 8.4	316.0	d) "C" approximation from extrudate swelling data
Av. mol. mass, $M_n \cdot 10^{-5}$	from LVN	5.8 $\sim$ 6.2 ^{a0}	4.1 $\sim$ 4.6	1.62 $\sim$ 1.78	1.40 $\sim$ 1.55	1.15 $\sim$ 1.25	0.92 ^{b0} $\sim$ 1.00	e) at 503K
Tensile strength, R_m , MPa	638	35	25.2 $\sim$ 35.0	32.6 $\sim$ 36.8	24.8 $\sim$ 30.1	23.2 $\sim$ 28.9	30.0	f) Tetralin, 393K, ml/g
Storage modulus, G'_{max} , MPa	2236	668	599	678	566	529	668	
Melting temperature range	=2171	441-444	436.5 $\sim$ 448	439.5 $\sim$ 444	443.5 $\sim$ 442.5	438.5 $\sim$ 439.5	401 $\sim$ 403	
ΔT_m , K								
Melt rheology @ 463K:								
Standardized for $\dot{\gamma} = 1$ s $^{-1}$								
—Viscosity, η_a , kPas ^{a0}	1703	12.5	11.5	10.8	13.3	9.66	6.80	
—Flow exponent, $n \cdot 10^{a0}$		431 $\pm$ 9.6	414 $\pm$ 5.5	415 $\pm$ 10	431 $\pm$ 6.8	471 $\pm$ 4.9	479 $\pm$ M.3	
—Elasticity, ψ_1 , kPas ^{a0}		(381) ^{e0}	(—)	(448) ^{e0}	(438) ^{e0}	(—)	(478) ^{e0}	
—Elasticity exponent, $m \cdot 10^3$		10.99	27.02	26.85	20.83	27.75	47.59	
—Flow activation energy, E_p , kcal/mole ($P_{12} = \text{const.}$)		1039.5	844.8	792.5	801.2	732.9	252.2	
Designation:								
		ASHOS 0	ASHOS 15	ASHOS 25	ASHOS 50	ASHOS 75	ASHOS 100	

Table 4. Characteristics of i-Polypropylene/LDPE^a, Blends—Type "a"

Characteristic (± standard error)	ASTM method D-	0 ¹	10	Blend composition in mass % of LDPE	80	100 ^b	Comments
Density, d_{25}^c , kg m ⁻³	1505-88	904.5	902.8	905.5	912.6	913.5	a) D 135, ml · g ⁻¹
Specific volume, V_{25}^c , cm ³ /g		1.318 ± .10	1.363 ± .027	1.501 ± .011	1.296 ± .038	1.289 ± .074	b) const. pressure viscometer HSV (l/d) = 16.7
Melt Flow Rate, FR, 463K, 5kG load	1238-73 (procedure)	5.11 ± .40	4.92 ± .70	4.08 ± .08	250 ± .70	1.67 ± .30	1.32
Melt Memory Index, MMI, %	1601-61 ^{a1}	152 ± 12	149 ± 8	160 ± 10	180 ± 11	182 ± 10	175 ^a
Limiting Viscosity Number, LVN		297	278	260	208	197	134
Melt Rheology, standardized characteristics @ 463K	1703-62 ^{a2}	83 ± 4	83 ± 5	84 ± 6	108 ± 5	124 ± 7	Supplier: 1) MALEN J 400 "MZRIIP" Plock, PL 2) Politen II 003/G0 ZCh "BLACHOWNIA," KEDZIERZYN/KOZLE, PL
—Viscosity, η , kilopascals		462 ± 10	466 ± 12	467 ± 13	489 ± 9	496 ± 13	"-annealed sample F = film sample
—Av. flow exponent, $\bar{n}$ · 10 ³		0.842 ± .07	0.851 ± .06	0.481 ± .08	1.253 ± .23	3.049 ± .41	91.9
—Elasticity, ϕ , 10 ⁴ Pas ³ or ϕ^0 · 10 ⁻³ , dynes · cm ⁻² · s ²		858 ± 20	816 ± 20	911 ± 50	798 ± 50	685 ± 46	557 ± 12
—Av. elasticity exponent, $\bar{m}$ · 10 ³		1.80	1.85	1.90	2.00	2.10	672 ± 18
Melt mixing torque, M, kg · m		a_0 ("P11")	a_1	a_2	a_3	a_4	2.40
Designation							a_{10} ("P")

tensile yield strength (R_{pl}). The relationships are subsequently used for computer drawing of the operational-surface graphs. In Fig. 10, these are shown for molding-grade Blenden-1040/W1 (upper row) and a film-grade LDPE: white areas with annotated mixing time ("t" in mins) outline T_b - P - t surfaces over which compounds of satisfactory characteristics, FR, MMI, d_{25} , and R_{pl} , are manufactured. Note that, for the iPP/LDPE blend, the accessible-mixing-parameters surface diminishes with increasing mixing time, in contrast to experience with LDPE melt homogenization (here, LDPE is that used as the blend component).

Dispersive melt mixing is routinely followed by laminar mixing in a long-screw extruder-pelletizer; in this stage of the manufacturing process, one can exploit the melt viscosity characteristics of a molten blend (Table 1, Eq 5) in order to predict goodness of mixing, expressed in terms of the weight-strain (WATS) concept of Pinto and Tadmor (11). Under simplifying assumptions, one may consider (for known screw geometry and a given melt-viscosity function for a blend) that it is feasible to evaluate goodness of mixing as a function of the extruder-mixer screw rotational speed, $\dot{N}$. The WATS- $\dot{N}$ relationship for an industrial mixer and blow-molding grade iPP/LDPE (Blenden PII020/D1) system is illustrated in Fig. 11.

Extrudate swelling, β , and, in particular, its rate dependence, $\beta(\dot{\gamma})$, are effective tools in both manufacturing and in processing operations development. Albeit the "processing applications" are more numerous, the application of extrudate-swelling-derived recoverable strain, γ (see Table 1), for an indirect check in blends morphology is important for manufacturing development. Using recoverable strain γ —shear stress- p_{12} plot (Fig. 12), one can distinguish between the interlocked (lamellar, stratified, or sandwich type-curve for 0.25 PP/0.75 HDPE blend in Fig. 12) and droplet/rod-in-the-matrix (curve for 0.75 PP/0.25 HDPE blend) morphologies (5a, 9). Examples of the respective morphologies are shown in Fig. 13 for polypropylene blends.

Applications of melt-rheology characteristics of the blends for processing and processability evaluation consist of the routine use of viscosity functions for process equipment and parameters design (11) and of somewhat less obvious exploitation of extrudate swelling and elasticity characteristics derived therefrom. Perhaps the most evident applications of extrudate swelling are in the development of a film-grade blend. Following experience with film-grade LDPE processability evaluation (43), one may exploit annealed extrudate swelling (especially that determined for very long (β_{∞}^0) or very short (β_{∞}^0) capillary extrusions (50)) for estimating extrusion-blown film thickness scatter, Δg (Fig. 14) and/or film haze, k^* , expressed here as the light-absorption coefficient (Fig. 15). Obviously, in order to establish such empirical relationships, it is necessary to evaluate β of the film-blowing process and the film quality for a comprehensive number of the "pilot" batches of the blend.

Parameters β_{∞}^0 , β_{∞}^0 , discussed above, are maximum

Table 5. Factorial Design Experiments: Mixer Parameters—Property Equations (48)

$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3$		
$b_0 = \frac{\sum_{k=1}^N y_k}{N}, k = 1.2 \dots N; b_i = \frac{\sum_{k=1}^N x_{ik}y_k}{N}, i = 1.2 \dots n; b_{ij} = \frac{\sum_{k=1}^N x_{ik}x_{jk}y_k}{N}, i, j = 1.2 \dots n, i < j;$		
$b_{\mu i} = \frac{\sum_{k=1}^N x_{ik}x_{\mu i}y_k}{N}, i = 1.2 \dots n, i < \mu$	n —independent variables in the factorial plan	
N —number of experiments		
FR = -1.038 + 0.036X ₁ + 0.983X ₂ + 1.404X ₃ - 0.007X ₁ X ₂ + 0.008X ₁ X ₃ - 0.253X ₂ X ₃ + 0.002X ₁ X ₂ X ₃ ; (Flow Rate, 463K, 5kG)		
X ₁ - temperature, T _b ; [°C]	X ₂ - ram pressure, p ₁ ; [kGcm ⁻²]	X ₃ - mixing-under-ram, t [min]
MMI = 123.1 + 0.3X ₁ + 9.2X ₂ - 1.5X ₃ - 0.07X ₁ X ₂ + 0.02X ₁ X ₃ + 0.03X ₂ X ₃ + 0.003X ₁ X ₂ X ₃ ; (Melt Memory Index)		
d ₂₃ ¹ = 0.83242 + 0.00058X ₁ + 0.01103X ₂ + 0.00948X ₃ - 0.00009X ₁ X ₂ - 0.00008X ₁ X ₃ - 0.00159X ₂ X ₃ + 0.00001X ₁ X ₂ X ₃ ; (Density)		
R _{plr} = 381.3 - 0.95X ₁ - 16.93X ₂ - 18.36X ₃ + 0.16X ₁ X ₂ + 0.16X ₁ X ₃ + 2.72X ₂ X ₃ - 0.02X ₁ X ₂ X ₃ . (Tensile Yield Strength)		

values within the shear range for which the extrudate swelling was measured. A somewhat less arbitrary swelling measure, which also displays satisfactory correlation with Δg and k'' in Figs. 14 and 15, is the free term in the semilogarithmic parabolic approximation:

$$\beta_{\infty}^* = A + B \ln \dot{\gamma} + C \ln^2 \dot{\gamma} \quad (8)$$

(for Eqs 1 to 7, see Table 1.)

Knowledge of the viscosity and elasticity (relaxation time) functions for a molten blend could also be employed for an estimation of the extrusion process stability, as expressed by the melt-temperature fluctuation, ΔT_m . It has been established for a number of screw geometries (51) and a range of extrusion process parameters that products of Deborah and Brinkman numbers

(45) (defined, respectively, as)

$$De = \frac{\tau}{t_r} \text{ and } Br = \frac{\pi^2 \cdot D^2 \cdot \dot{N}^2 \cdot \eta}{k \cdot \Delta T} \quad (9, 10)$$

(where t_r is process characteristic time, D is diameter, $\dot{N}$ is the speed of rotation of extruder screw, k is thermal conductivity, and ΔT is the barrel-screw temperature difference) the ΔT_m is related to the process stability through a reliable (correlation coefficient, $r = 0.93$) equation (52):

$$\Delta T_m = 5 \cdot 10^{-3} + 893 (Br \cdot De) \quad (11)$$

Since the admissible limits for temperature fluctuations for a number of high-rate extrusion processes (cable covering, film casting, etc.) are known, it is possible to estimate blend processability using its rheological characteristics and screw geometry.

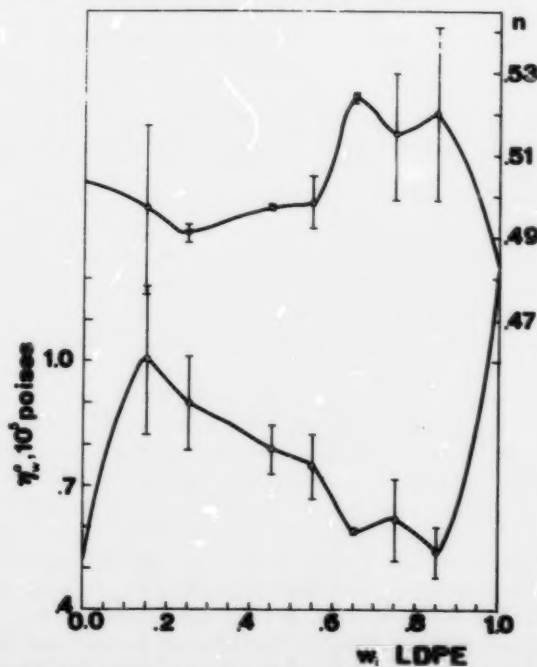


Fig. 6. Composition dependence of standardized melt viscosity, η^* , and its rate dependence, n (Table 1). Approximation "C," 463K, i-PP/LDPE (a) blend.

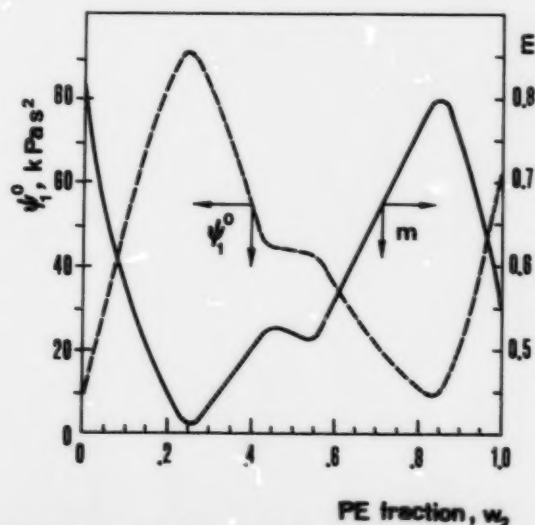


Fig. 7. Composition dependence of standardized melt elasticity, ϕ_1^0 , and the power law exponent, m . Approximation "C," 463K, "a" blend.

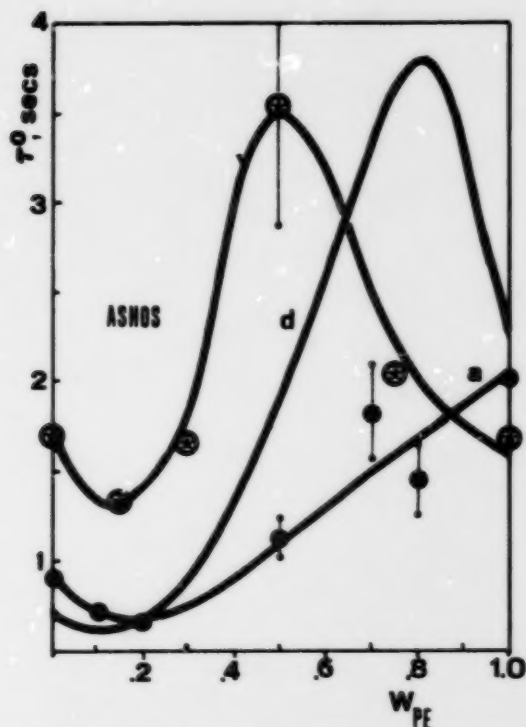


Fig. 8. Composition dependence of the characteristic relaxation time, τ^0 , 463K, approximation "A," polyolefin blends listed in Fig. 3.

Development of High-Strength, Heat-Shrinkable i-PP/LDPE Blend

Applications of the melt rheology data in the manufacture of industrial blends may be illustrated with development of a film-grade polypropylene/LDPE blend, Blenden®-PII020/F1 ("Blachownia," Poland). It is manufactured in a two-stage melt-mixing process, and the extrusion is blown into heat-shrinkable films using standard LDPE processing equipment.

Development of the blend was aimed at film-thickness reduction and was necessitated by requirements toward higher strength at shrink-packing oven temperatures. Composition of the blend was selected initially in close proximity to the particular rheology composition (PRC), at which both viscosity and elasticity are at a minimum (Fig. 1), viz. at ca. 90 wt. % LDPE. Melt-mixing process parameters were first selected by the factorial design experiments (J.S.W. high-speed, dispersive mixer) and by calculating the homogenizer-pelletizer (laminar mixer) performance using the melt-viscosity function for the blend (see, e.g., Fig. 11). The pelletized blend was then extrusion blown into films that displayed satisfactory performance characteristics (53). In-field packing tests, however, demonstrated that seal strength was too low. Notoriously poor heat sealability of polypropylene appeared to be the most obvious cause—in a microheterogeneous blend, most physical properties of the components are preserved (35). Indeed, the shift in composition toward higher LDPE content with simulta-

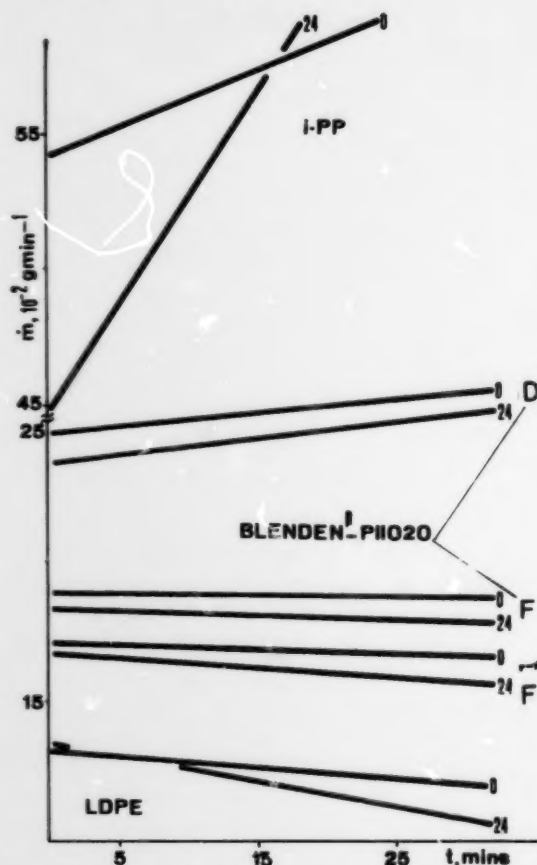


Fig. 9. Time-dependence of the mass flow rate, MSR at 463K for polypropylene, LDPE, and their blow-molding (designation/D1) and film-blowing (I/F1) grade commercial blends.

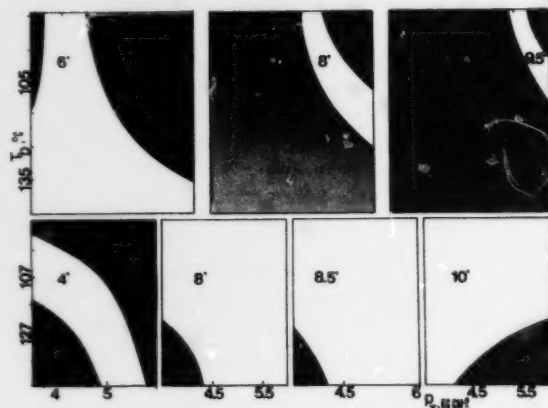


Fig. 10. Operation parameters for an industrial dispersive mixer: ram pressure- p_r , heating jacket temperature- T and mixing time, t , in mins. Unshaded areas designate admissible p_r - T - t combinations for manufacturing i-PP/LDPE, injection-molding grade i-PP/LDPE blends (top row), and for homogenization of film-grade LDPE (bottom row) (Courtesy Przemysł Chemiczny (Warsaw) 1976).

neous compensation for melt-viscosity increase with microadditions of a silicone oligomer (54, 55) resulted in a commercial blend fulfilling the performance requirement. The possibility of approximately 25 percent reduction in film thickness under the same per-

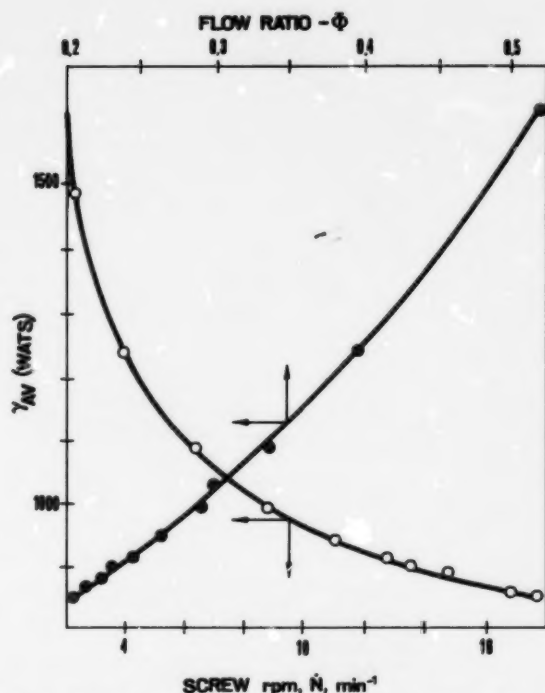


Fig. 11. Mixing efficiency of an industrial extruder-homogenizer expressed with weight-average total strain, γ_{AV} (11), as a function of the screw rotation speed, $\dot{N}$, and drag-to-pressure flows ratio, ϕ (Courtesy Academic Press, 1978 (5)).

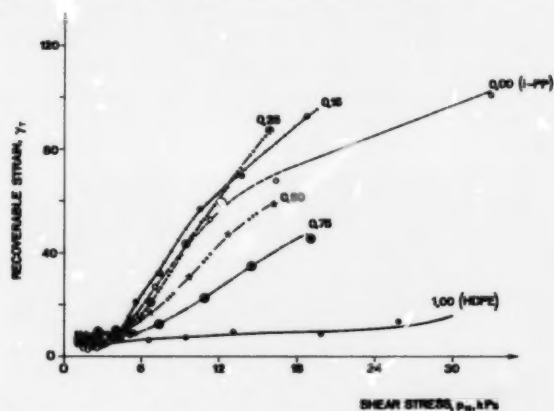


Fig. 12. Shear stress dependence of the recoverable strain, γ_r , as the criterion (5a, 9) for disperse vs. interlocked morphologies in i-PP/HDPE blends.

formance characteristic was ascertained (Fig. 16).

A similar procedure was used in the development of blow-molding grade HDPE/LDPE and iPP/LDPE blends for processing into 165 and 220 dm^3 barrels. Here, the development was motivated by substitution of HDPE; linear polyethylene grade for large blow moldings is rather expensive and sometimes not readily accessible.

CONCLUSIONS

Reliable (known confidence limits) melt-rheology characteristics are necessary in order to select a blend composition with regard to the particular rheology com-

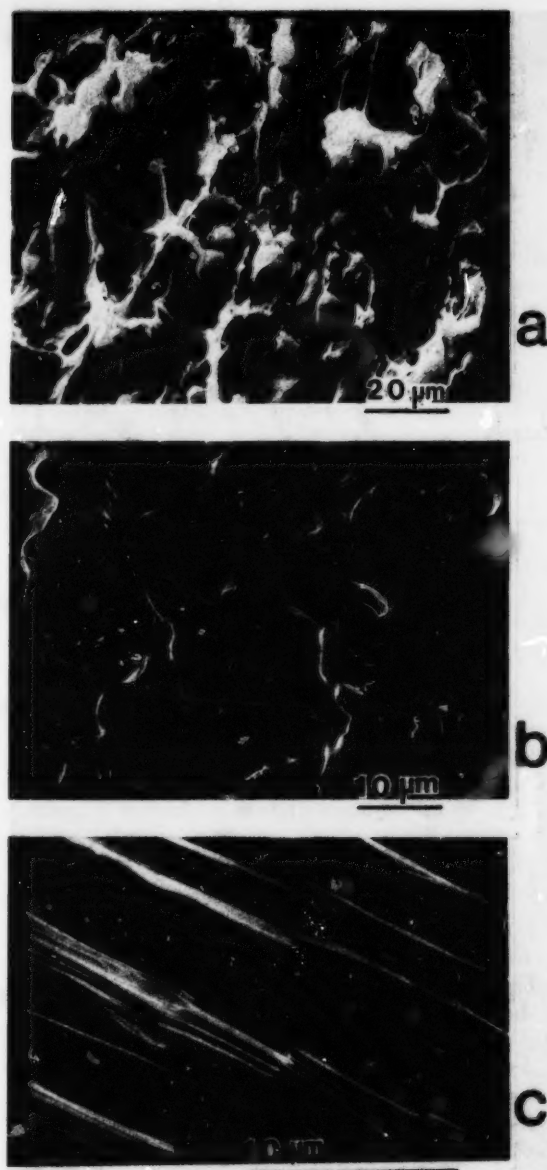


Fig. 13. Types of morphologies for binary polymer blends: scanning electron microscopy, freeze-fractured samples: a. emulsion type, dispersed morphology, bar—20 μm ; b. rods in matrix morphology, bar—10 μm ; and c. minority component forms thin sheets (plates) separating matrix—the interlocked morphology, bar—10 μm (Courtesy Mr. B. L. McGill).

position (PRC); i.e., the concentration range for which melt fluidity and compliance attain maxima. Further applications of melt rheology are in the design of manufacturing process and an evaluation of processability, as well as in quality control. Future developments in design of industrial polymer blends would involve control of their morphology, optimization of the melt-mixing process (aimed at minimizing energy requirements), and rationalizing three or more component blends with the statistical design approach (56).

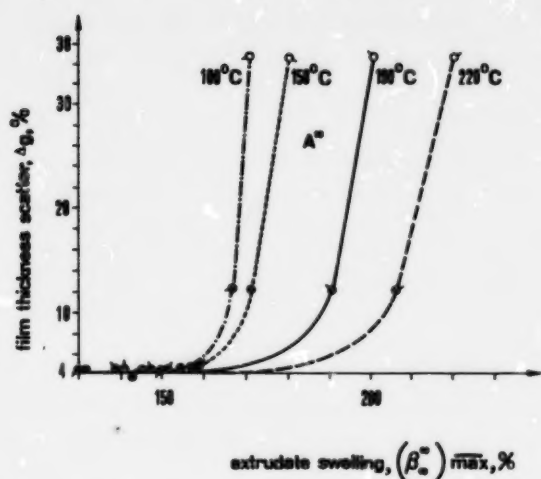


Fig. 14. Extrudate swelling as a criterion for the extrusion blow film thickness scatter, Δg . The swelling expressed with steady (β^*), and short duration (β_s^*) melt flow extrudates/die diameters ratios and with the first parameter of the logarithmic parabola approximation for β -shear rate relationship, A. (Courtesy Dr. L. Czarnecki, 1976).

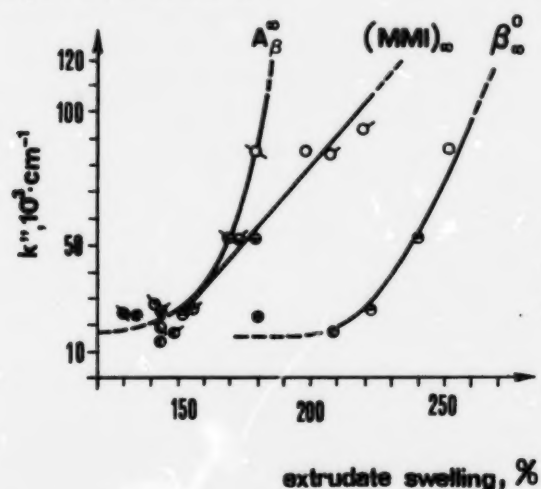


Fig. 15. Extrudate swelling as criterion for the extrusion blown film haze evaluation. Designation as in Fig. 14, k'' —visible light absorption coefficient as a measure of haze (Courtesy Dr. L. Czarnecki, 1976).

ACKNOWLEDGMENTS

Support of the Polymer Engineering Program at the University of Tennessee, which the author was happy to join as Research Professor at the kind invitation of Professor James L. White, is truly appreciated.

NOMENCLATURE

- a_i = iPP/LDPE blends (Table 4)
 "A" = least squares log. parabola for a rheological function (Table 1) taken over both low (e.g., rheogoniometer) and high (capillary viscometer) shear data
 A = logarithmic parabola (Eq 8) parameter
 b = exponent in the Clark-Oda-White Eq (Table 1 and (41))

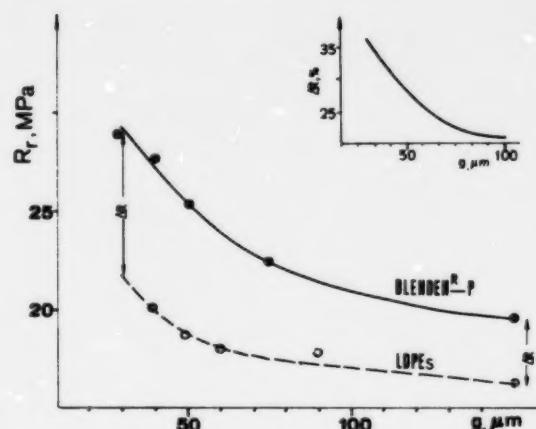


Fig. 16. Thickness dependence of the film-tensile strength: iPP/LDPE-blend film compared with LDPE films.

- B = logarithmic parabola (Eq 8) parameter
 "B" = the logarithmic parabola approximation over the low shear data
 Br = Brinkman number (Eq 10), dimensionless ratio of heat generation to heat conduction in a flowing polymer melt
 C = the logarithmic parabola approximation over the high shear data
 d_i = HDPE/LDPE blends (Table 2)
 d_{23}^A = density at 23°C
 De = Deborah number (Eq 9), the dimensionless ratio of characteristic (melt) relaxation time (e.g., τ^0) to a characteristic process time, t_r
 DCS = "discrete composition sampling" blends—laboratory melt mixed blends spaced at equal composition intervals (e.g., every 10 wt. %)
 FR = flow rate: the standardized (ASTM-D1238) melt-mass flow rate, g/10 min
 G = (apparent) shear modulus, taken as the ratio of shear stress to recoverable strain, Pa
 k = thermal conductivity (Eq 10), kcal/h °C m²
 k'' = visible light absorbance, cm⁻¹
 m = elasticity exponent (Eqs 2, 4, Table 1)
 MMI = melt-memory index, extrudate swelling as measured during FR test, percent
 MSR = melt stability ratio, slope of the FR-time plot
 n = viscosity exponent (Eqs 1, 3, Table 1)
 $\dot{N}$ = extruder's screw rotation speed, rpm
 PRC = particular (melt) rheology composition for which maximum and/or minimum of a rheological function (Table 1) is observed
 R_r = tensile strength, MPa
 R_{pir} = tensile stress at yield, MPa
 t_r = process characteristic time (e.g., melt residence in a die), s
 T_m = average melt temperature, K
 WATS = weight average total strain, established after Tadmor and Pinto for an extruder screw channel
 "wetting" components = the polymers forming appreciable interfacial layer upon melt mixing

- β_{∞} = extrudate swelling (i.e., extrudate to die (capillary) diameters/ratio), measured on annealed extrudate, percent
- β_{∞}^{∞} = as above for a very long capillary
- β_0^0 = as above for a very short capillary
- γ^0 = "standard" shear rate of 1 s^{-1} , to which all "standardized" rheological functions (η^0 , ψ_1^0 , N_1^0 , etc.—Table 1) are referred

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APPENDIX

Characteristic Relaxation Time as a Measure of Molten Blends' Deformability

An alternative way for evaluating composition dependence of blends viscoelasticity using standardized viscosity, η^0 elasticity, ψ_1^0 , and characteristic relaxation time, τ^0 :

where

$$\tau^0 = \frac{\psi_1^0}{2\eta^0} \quad (\text{A.1})$$

and

$$\psi_1^0 = N_1^0/\dot{\gamma}^2, p_{12}\text{-shear stress and } \dot{\gamma}\text{-shear rate} \quad (\text{A.2})$$

is to use reduced rheology characteristics (e.g. τ^0), expressed as the ratio of a characteristic for a blend, τ_b^0 , divided by the characteristic of a component, τ_1^0 .

Assuming validity of the relationship (13, 41):

$$N_1 = 2p_{12}\gamma, \text{ where } \gamma\text{-recoverable strain} \quad (\text{A.3})$$

At the standard shear rate, $\dot{\gamma}^0 = 1 \text{ s}^{-1}$, one has:

$$\begin{aligned} \tau_r^0 &= \frac{\tau_b^0}{\tau_1^0} = \frac{(N_1^0)_b/(N_1^0)_1}{(\eta^0)_b/(\eta^0)_1} \\ &= \frac{(p_{12}^0 \cdot \gamma^0)_b}{(p_{12}^0 \cdot \gamma^0)_1} \cdot \frac{(p_{12}^0)_1}{(p_{12}^0)_b} = \frac{\gamma_b^0}{\gamma_1^0} = \gamma_r^0 \quad (\text{A.4}) \end{aligned}$$

thence the reduced, characteristic relaxation time, τ_r^0 , being equal to the reduced recoverable strain of a blend, γ_r^0 , could be regarded as a representative measure of interaction intensity for the blend components. Plot of τ_r^0 vs. composition forms, therefore, is an additional check for the particular rheology composition(s) (PRC), as well as offering an estimate of melt deformability enhancement due to blending. In other words, τ_r^0 indicates how much is standard recoverable strain for a blend higher than the strain characteristic for the most elastic component of the blend.

Discussion—A. Plochocki

R. S. Porter. The paramount consideration is the viscosity match or mismatch of the two polymers involved in compatible disperse flow. In processing, mixing, extrusion, or injection molding, there is inevitably a wide range of velocity profiles. This is to say, an inherent tendency to separate, to stratify the blend by viscosity. It seems that there is an inherent complication of sizeable proportion in any of these considerations.

A. Plochocki. The whole reason for the use of rheology here is based on the fact that the two basic rheological quantities determine the properties of the blends. The viscosity ratio establishes the size of the phases; it is generally accepted in the literature that, in order to have a very fine dispersion of minor component, the viscosity ratio should be close to 1 (42). Unfortunately, we cannot confirm this. For the system polypropylene/rubber, we have a viscosity ratio of 25, and still, the dimension of the dispersed phase was within a few microns. We know, since the work of Starita, that viscosity ratio has a paramount importance in determination of the size. On the other hand, the *ratio of the elastic properties* determines the shape of the minor component. We checked and we found evidence supported the theory of Van Oene that, if you have a "proper" ratio of elasticities in the melt, then (in a given blend) you can have either a lamellar (stratified) structure or droplets in the matrix morphology. What I said is trivial, but I think that, in industrial applications, this is important. We do not know much about dispersive mixing which, together with the ratio of viscosity, establishes the size of the minor phase. Frequently, the recommendations based on laboratory data on the viscosity and elasticity ratios are invalidated to a large extent by an "improper" dispersive mixing process, which (in turn) depends on equipment and operation. Yet, to some extent, we can predict the morphology of a melt mixed blend.

L. A. Utracki. I support the statement. Demand for equal viscosity of the two components comes from homogeneous flow. In homogeneous systems, the viscosity vs. concentration usually go through a maximum. So the viscosity may increase, but it is a single-phase flow, anyhow. In cases of heterogeneous systems, most often there is a negative deviation from the linear composition dependence. In other words, even if you have the same viscosity of the two polymers, once you start blending, the viscosity falls down and, in the system,

one component flows faster than the other, which may lead to shear separation, stratification, etc. The only way that I know to overcome the problem is to enhance the interface interactions and generate the emulsion type of blends by enhancing the interaction between two phases.

A. Plochocki. I may add one comment. The viscosity ratio is changing with shear rate. You may start with a high rate but, at a certain stage of the process, it may be much lower. In trying to reduce the size, the critical part of the process has to be considered.

G. L. Bata. Can you improve homogeneity by simply increasing the back pressure on the extruder? The risk, of course, is that you will diminish output. If so, one could start off simply with blend of granules without preblending. This should be commercially more feasible.

A. Plochocki. Yes, by increasing the back pressure, you increase the total strain accumulated by the phases. You can make them thinner, more fine. Since the typical industrial level of production of blends is of the order of a few hundred tons a day, an operation of the type that you are suggesting poses, therefore, a financial risk. Such practice has support among some people, however. This is correct.

L. A. Utracki. In commercial operations, there are two ranges where the rate of shear is very important—for the film blowing, virtually zero rate of shear is important, and during the extrusion, where you have high rates of shear, $\dot{\gamma} = 10^3$ to 10^4 s⁻¹. For rheological measurements, it is important to evaluate the flow in the range observed in production. In your particular method of treatment, you are using $\dot{\gamma} = 1$ s⁻¹ as a sort of standardized rate. How can you get correlation with the process?

A. Plochocki. Thank you. In trying to be brief, I did omit important information. First of all, if you are developing a blend, you are developing it for a specific application. There are no universal blends. Because of my preoccupation with film, I was trying to illustrate the development of blends for this application. We developed a blend for injection molding, and the parameters that we used to characterize the blend were quite different. Coming back to the standardized viscosity or elasticity at $\dot{\gamma}^0 = 1$ sec⁻¹, you criticize it as taken at an unreasonably low level. I cannot very well agree since, as you recall, in the equation proposed by Prof. McKelvey, the standardized shear of stress or standardized viscosity is used as a dimensionless tool. You have this value, as well as the value of the exponent "n" (Table 1, Eq 3), and you can calculate the viscosity at higher or lower shear rate provided that you stay within the range of the rheological variables determined in the laboratory. If you move out of the range, then you are in danger because the parabola approximation is valid only within the experimental range. Within this range, you can estimate viscosity and elasticity within 20 percent of accuracy, using the standardized viscosity or elasticity and the respective power-law exponents. This is why one has to have four instead of just two parameters.

Economics of Polymer Blends

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Economic, technological, and regulatory pressures gradually narrow the chemical variety of polymers: in 1975, the market share of polyethylene was 40 percent, poly(vinyl chloride), 23 percent, polystyrene, 12 percent, and polypropylene, 11 percent, adding up to 86 percent of all thermoplastics (1-3). The same pressures compel the plastics processor to diversify formulations and production methods. He must resort to new materials (e.g., polymer blends, polymer alloys, and composites) and new methods of manufacture. In this work, the economics of blending will be discussed.

There are five reasons to employ polymer blends:

- higher performance at a reasonable price,
- modification of performance as a market develops,
- extending the performance of expensive resins,
- re-use of plastics scrap,
- generation of a unique material as far as its processability

and/or performance are concerned.

In Canada, the cost of blending varies from 8 to about 20 ¢/lb, depending primarily on the volume and the kind of material. The cost effectiveness depends on the total technical and economic environment in which the manufacturer operates; it has to be computed for each case separately. In the text, guidelines and examples are provided.

INTRODUCTION

Polymer blends (Pbl) are mixtures of chemically different polymers and/or copolymers. Pbl are mainly multiphase systems with the structure dependent on composition and processing conditions. A few miscible blends are known (e.g., PPO/PS) where phase separation takes place only *above* the critical temperature. Polymer alloys (Pal) are a class of pbl in which a large interpenetration of domains is secured by either chemical or physical means. In industry, the term "polymer blend" is also used for dry blends of polymer compositions; viz., mixtures of high- and low-density polyethylenes or dry blends of poly(vinyl chloride) formulations. For this reason, it is useful to keep a strict distinction between the "blends"—a direct result of the blending action, and "alloys"—the final blend of well-defined morphology and set of properties.

Polyblends are mixtures of structurally different homopolymers and/or copolymers. They are prepared (4, 5) by:

- mechanical mixing in extruders, compounders, intensive mixers, motionless mixers, cryogenic grinders,
- dissolving the ingredients in common solvent,
- latex blending, and

- dissolving or dispersing one polymer in the monomer of another, then polymerizing.

In large volumes, pbl and pal are mainly prepared by the first method. At high temperatures and shear stresses, in the presence of reactants, one may interlace the polymer molecules to form alloys. However, when the resins are partially miscible ("compatible"), or when a compatibilizer is added, physical alloying may provide equally good results. It is important to remember that, for optimum performance, an optimal degree of dispersion must be achieved; overdispersing will reduce the technical parameters similarly, as underdispersing does.

The number and variety of commercial blends is limited (e.g.: PVC/Acrylic, PVC/ABS, PVC/CPE, PC/ABS, PSF/ABS, PPO/PS, PET/PBT, PPS/PTFE), but the production of pbl, already about 10 percent of all thermoplastics, is increasing rapidly. Most blends are introduced for short runs, for specific applications, by small or medium-size plastics manufacturers, with or without help from a resin producer or compounder, often without patent protection. The key to blending is economic viability. As raw material costs contributes from 35 to 80 percent of that of the finished article, the future of polyblends lies in their attractive cost/performance ratio. The world plastics production and Canadian level of consumption are given in Table 1.

Table 1. Production and Use of Plastics (1-3)

	1963	1975	1990*
World plastics production (MM tons)	13	47	166
Thermoplastics (%)	66	75	82
Annual growth rate (%/year)	15	11	9
Canadian consumption (% of total plastics)			
Poly(ethylene), LDPE + HDPE	34	37	35
Poly(propylene)	1	7	9
Poly(vinylchloride)	16	13	13
Poly(styrene)	7	9	14
All four	58	66	71
All four as % of thermoplastics	74	84	88
Annual growth rate (%/year)	15	11	9

*Projected

CLASSIFICATION

Pbl/Pal are classified from the point of view of: *miscibility* (miscible, "alloys," immiscible), *morphology* (amorphous, semicrystalline, isomorphous, complexing), *method of preparation* (mechanical, solvent-cast, latex, and chemical) and *function* (flammability, impact strength, heat distortion . . .).

Miscibility (6, 7). Only a few polymer blends are truly miscible, to the molecular scale; poly(phenylene oxide)/polystyrene (PPO/PS) or poly(vinyl chloride)/polylactone (PVC/PCL) are such systems. The miscible systems exhibit a single-glass transition temperature, T_g , located between the T_g s of the two components. These blends can be expected to appear and behave like single-component polymers; they will be transparent and can be molded without streaking. The heat distortion temperature of miscible blends varies smoothly with composition and thus is easy to predict and control.

Most polymer mixtures are immiscible, forming multiphased structures. The interface between two adjacent phases is not clear-cut. There are composition gradients whose level depends on the intensity of mixing and on the solubility of the polymers. One is often forced to consider these gradient regions as a separate, third phase (or "interphase"), the properties of which determine the final performance of the blend. The compatibilisation may be necessary in order to "decrease the degree of immiscibility" or to "improve compatibility" (7). Blends exhibiting low or partial miscibility are the most common in commerce. Some examples are PVC/ABS, polycarbonate/ABS, and PVC/acrylic. Because of the multiphase nature of these blends, opacity is the rule, and injection-molded parts may show swirl and other patterned surface imperfections. In most cases, the physical properties of polymer blends depend on the degree of dispersion. The blends are tough, mainly because of the intrinsic strength of the components combined with extra energy-dissipation mechanisms at the component interface. Permeability to gasses also seems to depend on the phase size (8). The most successful polyblends are the multiphase Pals with relatively extensive interpenetration zones (9-13).

Morphology (4). Here, Pbls can be divided into four categories: mixtures of amorphous polymers, mixtures of amorphous and semicrystalline polymers, mixtures

of crystalline polymers, and mixtures of polymers that form complexes.

Most of the miscible systems belong to the first and fourth; viz., PS/PPO and poly(vinyl pyrrolidone)/poly(acrylic acid), respectively. In the second, the miscibility is limited to the melt and amorphous phase; on cooling, the semicrystalline polymer partially separates and crystallizes. In the third class, most systems are immiscible. However, there are isomorphous systems; viz., poly(vinyl fluoride)/poly(vinylidene fluoride), which not only are miscible in the melt and the amorphous phases but also are able to cocrystallize in the lattice intermediate between those of the neat resins.

The complexing Pbls form a special class. Here, the segmental interactions (e.g., acid/base, ionic, hydrogen, complexing) lead to molecular, stoichiometric associations. These usually show higher T_g , better impact properties, poor solubility, clarity, and substantially modified gas permeability.

Method of preparation (1, 4, 5) leads to the classification as shown in Fig. 1. Commercially available polyblends are almost exclusively mechanical polyblends. Usually they are prepared either on an open roll, in an extruder, or in a suitable intensive mixer. The processing temperature must be well above the glass transition temperatures (T_g) of each of the constituent polymers for mixtures of amorphous polymers and for the melting temperature (T_m) for mixtures containing semicrystalline polymers.

Depending on the thermal stability, the high shear involved during processing can initiate polymer reactions due to the formation of free radicals. The free radicals can, in turn, react with different polymers present, resulting in true chemical grafts. Such mixtures are referred to as polymer alloys (6). The distinction between blend and alloy is quantitative and refers to the extent of interpenetration of domains. Besides grafting, the addition of compatibilizers (e.g., graft or block copolymers) of a mutually "compatible" plasticizer or polymer may lead to the formation of alloys. In short, alloying is related to the improvement of miscibility of the two neat components by mechanical or chemical means.

Generally, blending technology rests on the premise of property additivity, although (strictly speaking) the additivity principle is valid for miscible polyblends only. For these systems, such properties (P in Fig. 2) as

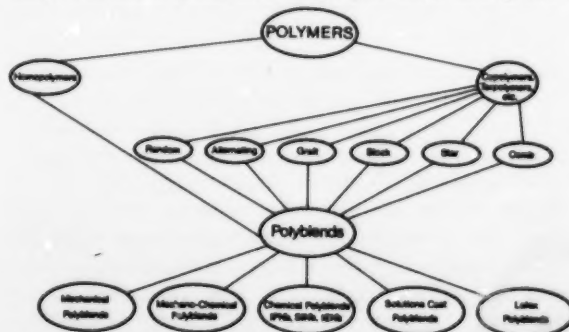


Fig. 1. Classification of polymer blends by the method of preparation (4).

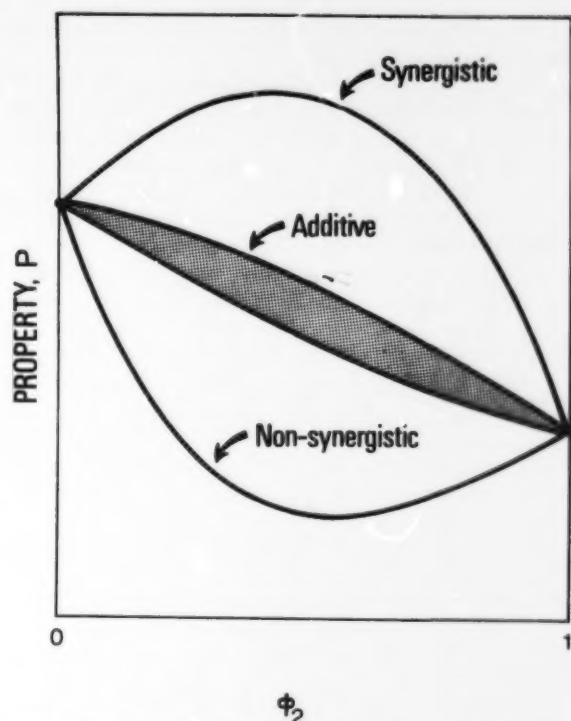


Fig. 2. Property-composition dependence for a miscible polyblend. There is a range of values within which the additivity principle is presumed to be obeyed (4).

T_g , density, refractive index, dielectric constant, thermal conductivity, heat capacity, thermodynamic properties, elastic moduli, viscosity of liquid mixtures, and surface tension of liquid mixtures follow the dependence (9):

$$P = P_1\phi_1 + P_2\phi_2 + I\phi_1\phi_2 \quad (1)$$

where P is the property of interest, ϕ is the composition, and I is an interaction term that can be positive, negative, or zero.

In the case of immiscible polymer blends (see Fig. 3), another semiempirical mixing rule is obeyed by such properties as elastic moduli, electrical conductivity, thermal conductivity, dielectric constant, thermal expansion coefficient, diffusion coefficients, and the viscosity of suspensions (9):

$$\frac{P}{P_1} = \frac{1 + AB\phi_2}{1 - B\psi\phi_2} \quad (2)$$

where $A > 0$ depends on the shape and orientation of the dispersed phase and the nature of the interface, B is a function of A , P_1 , and P_2 , and ψ is a reduced concentration term that is a function of the maximum packing volume fraction ϕ_m . However, for immiscible blends, the additivity rule has also been used to calculate such properties as moduli, impact strength, thermal and oxidative resistance, processability, environmental weatherability, color, hardnesses, heat resistance, flame retardance, domain morphology, thermal expansivity, thermal conductivity, compressibility, and refractive index. For a summary, see Table 2.

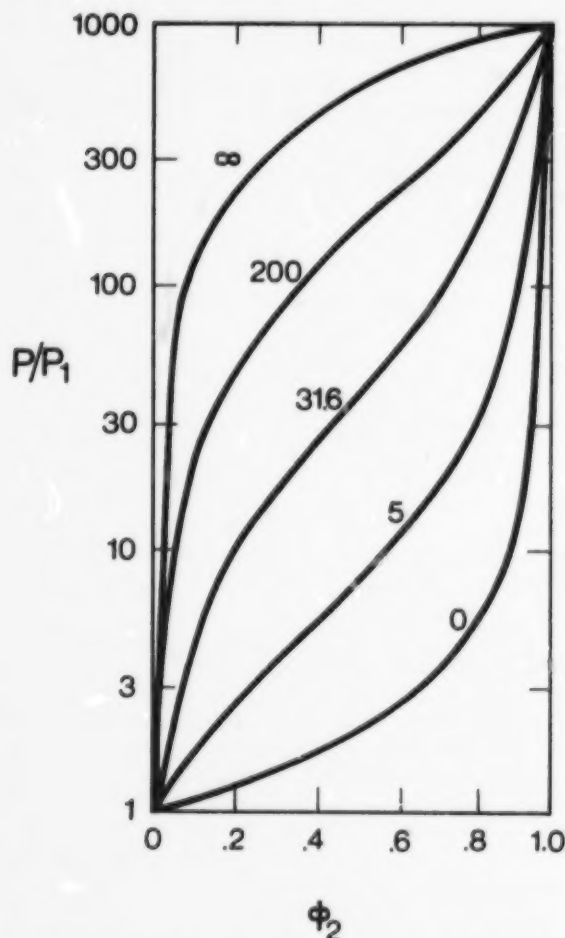


Fig. 3. Semilogarithmic plot of Eq 2 (with $\psi = 1.0$) for various values of A illustrating the possible patterns of property dependence on composition for an immiscible polyblend (9).

Function (1, 5). A successful polyblend is a cost-effective mixture of a basic polymer with another one, which may be considered an additive, affecting a particular aspect of performance without deleterious effects on the others. For example, PVC can be considered a flame-retarding additive for ABS or acrylic. Polysulfone and polycarbonate can be considered as heat distortion modifiers for ABS, while nitrile rubber is a plasticizer for PVC. This is summarized in Table 3. In general, the more functions the polymeric additive serves, the more successful the blend.

PERFORMANCE OF BLENDS

The P vs. composition dependencies, Eqs 1 and 2, are good general rules to start with. At the next stage, the formulator looks for synergism in T_g , mechanical properties, etc. However, all curves shown in Fig. 2 can be advantageous in specific cases. Positive deviations from linearity have been observed in the composition dependence of tensile strength, viscosity, elastic moduli, and the flexural strength of a miscible mixture of a brittle polymer with a ductile polymer. They represent the most sought-after type of dependence. The additivity rule is very advantageous for the compounder who

Table 2. Calculation of Polyblend Properties via Equation 1 or 2

No.	Property	Miscible blends	Immiscible blends
1.	Thermodynamic properties (compressibility, thermal expansion, heat capacity, thermal conductivity, surface tension. . .)	1	2,(1)
2.	Electrical properties (dielectric constant, conductivity. . .)	1	2
3.	Rheological properties (moduli, viscosity, diffusion, permeability. . .)	1	2
4.	Diverse:		
(a)	Glass transition temp.	1	—
	Refractive index	1	—
(b)	Density	1	1
	Weatherability	1	1
	Heat/flame resistance	1	1
	Processability	1	1
	Hardness	1	1
	Color	1	1,(-)

Table 3. Classification of Blends by Function of the Additive (5)

Function	Basic Resin	Additive
Impact modifier	PVC	ABS, EPDM
	PP	EPR, EPDM
	PE	PBR,
Heat-distortion modifier	PS	PPO
	ABS	PSF
	ABS	PC
Plasticizer	PVC	Nitrile rubber
	PVC	Ethylene copolymer
Opacifier	PE	PS
Flame retarder	ABS, acrylic	PVC
Process aid	PVC	Acrylic, CPF.
Extender	Nylon 6	Ethylene copolymer
	PPO	PS
	PE	PP
	PC	ABS
	PSF	ABS
	PBT	PET
Stabilizer	Polyester	Acrylic
	PPO	PS
	SAN	Polyolefin

wants to fine-tune the performance of the formulation to the client's specification. Negative deviations from the additivity rule are most common for the rheological functions of molten, immiscible polymer blends (13, 14); obviously, negative deviation in melt viscosity facilitates processing and results in a better product.

The dependencies shown in Fig. 3, especially those for $A = 0$ and ∞ , may represent the highly desirable case of engineering resin diluted with inexpensive polymer.

Virtually always, the decision "to blend or not to blend" is taken considering specific performance requirement and the actual financial situation; discussing performance without considering the cost (and vice versa) is meaningless.

COST CALCULATIONS

The material cost of Pbl/Pal, \$, can be calculated as:

$$\$ = K + \sum_i w_i \$_i \quad (3)$$

where w_i and $\$_i$ represent the weight fraction and price per pound of the components, respectively, and K is the compounding cost per pound. In Canada, for large-volume compounding in large-scale continuous process equipment (*viz.*, twin-screw extruder or Farrel Continuous Mixer), K varies from 8 to 12 ¢/lb; for small-scale, or for batch blending (*e.g.*, in a Banbury Mixer), the cost may escalate to 20 or even 25 ¢/lb. An excellent review on the compounding cost in the U.S.A. can be found in (15). The author calculated $K = 1.0$ to 22.5, depending on the production rate (10,000 to 250 lb/h, respectively). Considering the continuous *vs.* the shift mode of production, he arrived at a very substantial difference for large-scale production (*e.g.*, 1.0 *vs.* 2.2 ¢/lb at 10,000 lb/h level), but rather small for low production rates: 22.5 *vs.* 26.5 ¢/lb for 250 lb/h.

In Canada, the five leading compounders (Argo Plastics, Aclo Compounders, Canadian Fibrefil, Kayson Plastics, and A. Shulman Canada) manufacture about 60 to 80 MM (lbs/y) (16); at this level, the estimated cost of equipment (per company) exceeds \$3MM and the minimum compounding cost, 6 ¢/lb (in 1982 Can. \$). Domestically, the largest-volume blends are those containing polyolefins; *viz.*, polyethylene blends (high- with low-density) and rubber-modified polypropylenes. The U.S. consumption of polyblends is listed in Table 4.

Equation 3 can be used to evaluate the cost effectiveness of the in-house preparation of blends. Starting with Fig. 4a (*i.e.*, ABS/PVC system), one can see that in-house blending for high-PVC content formulas is cost effective. This means that, if impact modification of PVC is the desired property, blending is more profitable. On the other hand, if a decrease of ABS flammability is the goal, the buying of a commercial blend will

Table 4. U.S. Thermoplastic Alloy Consumption: in 1978 and 1983 (MM lb) (16)

N°	Blend	1978	1983	Annual Growth Rate (%)
1.	Large volume:			
	Rubber-Modified PS	2,033	2,913	7
2.	Intermediate:			
	PVC	269	467	12
	ABS	118	238	15
	Modified PPO	121	205	11
	TOTAL	508	910	12
3.	Emerging:			
	Acetal, Polycarbonate	14	40	23
	Polysulfone, others			
4.	Newest:			
	PBT/PET,			
	PET/NYLON,			
	NYLON/EPDM,			
	PC/ABS, PE,			
	Engineering resins/SBS			
	Epoxy/polyester			
	GRAND TOTAL:	2,718	4,162	9

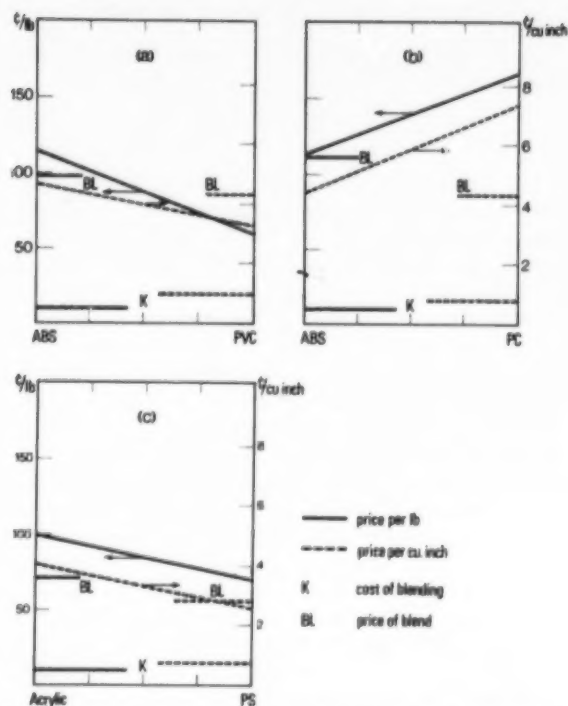


Fig. 4. Blending cost estimation for ABS/PVC (a), ABS/PC (b), and acrylic/PS (c). Solid lines refer to cost-per-weight (U.S. ¢/lb); broken lines refer to cost-per-volume (U.S. ¢/cu. in.). K indicates the assumed blending cost of 20¢/lb. "BL" indicates price of commercial blends.

make better sense. The case of ABS/PC on Fig. 4b is quite clear—buy it; both prices, per weight and per volume, are below the expected cost of in-house blends within the full range of compositions. In the case of Acrylic/PS, Fig. 4c suggests a potential saving for high-PS-content blends, but only for the price-per-volume comparison. Even at this limit, the savings are marginal.

A similar type of economic analysis should be made for all newly developed blends. In this case, the cost of blend must be compared with the price of the resin it is supposed to replace. Frequently, the decision is taken on the basis of cost savings, based on the performance of the finished article.

COMMERCIAL BLENDS

In Table 5, some commercial polymer blends are listed. In Table 6, examples of the property differences between the neat polymers and their commercial blends are given; the basic properties are underlined. The choice is to be made on the basis of price (or cost) of resins, as well as on their properties. The behavior of the basic types of blends will be discussed now in greater detail (4).

Polyblends Containing PVC

PVC is flame-retardant, relatively low-cost, thermally unstable, and a relatively brittle resin. On the other hand, ABS is relatively ductile and thermally stable, but it is not flame-retardant. The mixtures of ABS

and PVC at the proper compositions yield polyblends with improved heat distortion, thermal stability, excellent impact strength, chemical resistance, and flame retardance. The blends offer better gloss surface appearance than comparable flame-retardant materials. ABS/PVC polyblends were first introduced commercially in the 1960s by B. F. Goodrich (see Table 5). They are used in electrical appliances, automotive and building products, sanitary wares, etc.

Another important class of PVC polyblends are those containing PMMA, a material with relatively high heat-distortion temperature, which show high impact strength, excellent thermoforming characteristics, and chemical resistance. Addition of PMMA to PVC also improves its heat distortion and thermoforming characteristics. The presence of PVC at moderate concentration makes it possible to achieve good flame retardancy. These polyblends find applications in industrial appliance housings, fume ducting, aircraft interior components, industrial wall panels, truck cargo liners, and seat backs (17, 18). ABS/PVC blends could replace NORYL in 25 percent of its applications (19, 20), especially since the growth rate of the PPO/PS blend seems to be slowing (21).

Polyblends Containing ABS

Aside from the above ABS/PVC blends, there are commercial blends of ABS with PC, PSF (see Table 5), and thermoplastic PU. All are immiscible. The ABS/PC blends retain many of the best characteristics of both polymers: high notched-impact strength (particularly in thicker sections), excellent heat resistance, good processing characteristics, lower susceptibility to environmental stress cracking than PC, and low cost (see Table 6). Applications include electrical switches, electrical connectors, safety helmets, food service applications, pump parts, various specialty electronic applications and functional components, such as blower housings, calculator recharger housings, automotive backlight housings, kitchen aids, personal care articles, and power tools. The FORMACAR was the first car with a chassis and body frame made of an ABS/PC blend (22).

Polyblends Containing PS

Polystyrene (PS) blend with poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was developed in 1965 by General Electric and, since then it has been sold under the name of NORYL. It is a tough, rigid material that maintains excellent mechanical and electrical properties over a wide temperature range and exhibits good dimensional stability, with low creep and low moisture absorption. The major application for NORYL is in appliances, communications, business machines, automobiles, television components, electrical construction, specialty products, and cold- and warm-water applications. Foamable grades of NORYL find use in large housings and sound-deadening applications.

PS is also used in mixtures with elastomers and polyolefins. It has been known that blends of crystal PS are useful only when the volume fraction of the elastomer exceeds 25 percent (23). The elastomer may be either a

Table 5. Commercial Alloys and Outstanding Properties (5)

Composition	Typical Brands	(Manufacturer)	Outstanding Properties
PVC/Acrylic	Kydex Acrylvin DKE 450	(Rohm and Haas) (Gen. Tire & Rub.) (Sumitomo)	Flame retardance, Impact and chemical resistance
PC/ABS	Polydene Bayblend Cycloy EHA	(Schulman) (Mobay) (Borg-Warner)	Lower cost, HDT=104°C Notched-impact resistance, hardness, distortion temp.
PP/EPDM	TPR	(Du Pont)	Improved low-temperature impact and flexibility
SAN/Olefin PVC/ABS	Polyman 552 Polyman	(Schulman) (Schulman)	Weather resistance Flame resistance, self- extinguishing
ABS/PSF	Abson Cycovin KAF Kralastic FVJ Mindel A650	(Abtec) (Borg-Warner) (U.S. Steel) (Union Carbide)	Impact resistance, Improved processability
PET/Acrylic Nylon/elastomer PBT/PET	Arylon Ropet Zytel ST-801 Valox 800	(U.S. Steel) (Rohm and Haas) (Du Pont) (GE)	Lower cost, more uniform than former Arylon T
PPS/PTFE PPS/nylon Acrylic/PBR	BR 47, 48 XT Polymer	(also, GAF, Celanese) (Phillips) (Phillips) (Am. Cyanamid)	Notched Izod= 17 Lower cost
PPO/PS	Noryl	(GE)	Lubricity Clear, impact resistant blow-molding resin Lower cost, improved processability.

Table 6. How the Alloys Differ from the Base Resins (22)

Property	ABS (High-Impact)	Poly- carbonate	ABS-poly- carbonate	PVC	Acrylic	PVC- Acrylic	PS	PPO	PS/PPO
Specific gravity	1.02	1.2	1.04	1.35	1.18	1.35	1.06	1.06	1.06
Tensile strength, psi	5000	9500	6200	7000	10,000	6,500	4,750	10,500	9,500
Tensile modulus, 10 ⁶ psi	3.0	3.5	3.7	4.0	4.5	3.4	3.0	3.7	3.5
Impact strength, ft lb/in.	6	15	10	0.5-10	0.5	15.0	1.2	1.6	3
Heat deflection temperature, ° @ 255 psi	86	132	105	66	85	75	88	192	129
Flammability	Slow burning	Self-extin- guishing	Slow burning	Self-extin- guishing	Slow burning	Non burning	Slow burning	Non burning	Non burning
Price(U.S.\$/lb)	0.94	1.44	1.12	0.39	0.81	0.98	0.51	2.09	1.31

"conventional" rubber or a thermoplastic rubber of SBS or SIS type. Obviously, the addition of this amount of block polymer would be uneconomical. The system is immiscible, with rubber domains dispersed in a PS matrix. In Table 7, an example is given of the improvement of impact strength by the addition of SBS to HIPS (containing 25 percent rubber) and to its mixtures with crystal PS. In all cases, the impact properties are greatly improved. Polyblends PS/PE are being investigated by people from academia (24, 25), as well as by those from industry (26). The main reason for this interest is a large volume of industrial mixed scrap that has to be recycled.

Polyolefins Blends

These systems were recently reviewed in reference (26), where a list of 124 patents (since 1962) is given. Of these, the broadest category is PP/PE (52 patents), followed by a side group of polyolefins with other polymers (EVA, PC, PET, PPO, HIPS, SBS, PIB, PS, PDMS, etc.) (37 patents), the linear/branched PE (18 patents) and, finally, polyolefin/polyamide blends (17

patents). More recent information can be found in Refs. 25-29.

METHODS OF MANUFACTURING POLYMER BLENDS

Preparation of Pbl has not been sufficiently treated in the literature. Significant property variations are possible (30) for a given blend, depending upon the details of the compounding process. Mechanochemical reaction that could lead to graft copolymers of the two components have been discussed by Casale and Porter (31). Peroxides seem to enhance this process (32). Reactions that form oxygenated groups on both components may also lower interfacial tension and promote interpenetration. The presence of oxygen during the alloying process has been reported to be beneficial (32). In some cases, such as with poly(butylene terephthalate)/phenoxy, grafting by the transesterification is certain; the extent of reaction depends on temperature, time, and catalyst (33).

For alloying, high shear equipment is necessary. The equipment should control the temperature of the melt

Table 7. Properties of High-Impact Polystyrenes (23) and Blends with a Block Copolymer

A. COMPOSITION (parts of total)												
Shell high-impact polystyrene 338	100	97.5	95	100	95	90	80	100	60	40	30	40
S-B-S KRATON 2103	0	2.5	5	—	—	—	—	—	15	15	15	10
S-B-S KRATON 1101	—	—	—	—	5	10	20	—	—	—	—	—
Shell Polystyrene 202	—	—	—	—	—	—	—	—	40	60	70	60
B. PROPERTIES—EXTRUDED sheet												
Melt flow, cond. g (gm/10 min.)	3.15	3.95	4.65	3.0	3.2	3.1	2.7	4.1	7.0	7.5	6.6	6.0
Tensile yield strength (psi)	2950	2800	2850									
Tensile at break (psi)	2750	2500	2500	3500	3100	2800	2500					
Elongation at break (%)	40	40	55									
Gardner gloss (60°) (%)	17	17	24									
Thermoformed bottles												
Splitline	5	7	9									
Impact resistance (%)												
50 in. drop	60	100	—									
85 in. drop	32	96	96									
26 in. drop	—	—	—					75	395	225	105	50
Heat distortion temperature (°F)				189	188	188	186					
Izod impact strength												
@ 73°F (ft-lb/in.)				1.6	2.4	3.9	6.0					
@ 0°F (ft-lb/in.)				1.1	1.3	1.6	4.0					
Flexural modulus (psi · 10 ⁻³)								3.05	2.86	2.82	3.18	3.45
Flexural yield strength (psi)								5900	5800	6220	6850	7230
Gardner gloss, 60° (%)								79	84	95	96	95
Hardness, (Rockwell R)								100	87	89	93	98
Vicat softening point, (°F)								201	207	210	212	209

and limit its exposure to oxygen. The following mixers are often used:

- Banbury mixer (34)—primarily for polyolefins and rubbers.
- Farrel Continuous Mixer (FCM) (35)—similar in action and use to the Banbury, but designed for a continuous process.
- Corotating twin-screw extruder (36)—customized by fitting together various screw and kneading sections to suit particular resin/user needs.
- Specially equipped, single-screw extruders with shear enhancing devices—pins, mixing heads, gear pumps etc.
- Another method of mixing of polymer melts is by means of motionless mixers (37).—The principle is to divide the flow stream using a series of elements of opposite twist direction. This mixer has been used; e.g., by Han, *et al.* (24), for PS/PP and by Schott, *et al.* (38), for SAN with rubber blending.
- Gelimat—high-speed automatic mixer developed by Carlew Chemicals Ltd. (39) can also be used as an efficient compounder for Pbl/Pal. The machine is based on self-heating of the resins up to the desired temperature. The rotor blade tip speed is as high as 45 (cm/s), cycle time is less than 15(s), and the output capacity is up to 130 (kg/h) from one(1) capacity machine. A continuous Gelimat has also been designed.
- Short, multi-flight screw extruder (L/D = 5)—has been developed by C.R.I.F. in Belgium (40) specifically for blending thermally sensitive materials. The residence time is kept below 20s. Due to the high shear field, a good dispersing of incompatible polymers has been reported.

As stated before, melt blending is only one of many methods; it is the most widely used. Commercial blends are also prepared by *in-situ* polymerization; this

method is used predominantly for interpenetrating polymer networks (IPNs) or simultaneous interpenetrating networks (SINs), where the resulting cross-linked blend cannot be processed further except by machining (41, 42).

The cryogenic or impact grinders may also be used for preparation of Pbl. One can premix or postmix the ingredients. The resulting material can have well-defined particle size and particle size distribution. The cost in large volume is 10 to 15 ¢/lb; i.e., slightly higher than conventional compounding. The benefits are absence of thermal degradation and a good control of dispersion, which lead to improvements in Pbl performance. The disadvantages are absence of alloying and the need for modification of the processing equipment; viz., feed and melt homogenizing devices.

PATENTABILITY

M. T. Shaw (5) analyzed 59,439 patents, from which only 27, or 0.05 percent, dealt with polyblends; of these, 22 referred to composition, 3 to process, and 2 to application. The most frequently quoted improvements were of impact, 6, and processing and use of extender, both 4.

In the recent past, the trend toward patenting seems to have accelerated (see Table 8); at least 14 patents were published in 1981. It can be seen that, in most cases, the blend contains some kind of copolymer, that the most frequent improvement is in the impact performance, and that, more often, the patent for composition stresses the method of blending, not necessarily disclosing it.

EXAMPLES

The following examples of successful, cost-efficient blending are given to illustrate the use of the method. Of all the reasons for blending, scrap re-use, modifica-

Table 8. Example of Recent U.S. Patents on Polymer Blends

1.	3,825,622	1974	L. M. Robeson, <i>et al.</i>	Union Carbide	PVC/lactone	Impact modification
2.	3,873,667	1975	R. J. Preto, <i>et al.</i>	Continental Can	Polyolefins/nylon	Gas permeability
3.	3,920,602	1975	W. T. Freed	Celanese	Nylon-6,6/polyphenoxy	Tensile properties
4.	3,937,757	1976	W. Seydl, <i>et al.</i>	BASF	PBT/PE	Electrical tracking resistance
5.	4,122,131	1978	J. Bussiuk, <i>et al.</i>	GEC	PC/PE/SBS	Impact strength, processability
6.	4,126,602	1978	G. Salee	Hooker	PET/rubber	Hydrolytic stability
7.	4,146,586	1979	R. E. McConnell, <i>et al.</i>	Eastman	PET/PP	Melt adhesion
8.	4,146,589	1979	R. C. Dupré	Monsanto	PS/rubber	Toughness and gloss
9.	4,156,703	1979	W. H. Harrop	Rohm & Haas	PE/PET acrylate	Processability
10.	4,164,600	1979	K. W. Yung, <i>et al.</i>	Monsanto	PBT/polyactam	Low bonding T
11.	4,174,359	1979	P. Sivarama, <i>et al.</i>	Mobay	PC/halogen. comp.	Flammability
12.	4,179,422	1979	H. S. Makowski, <i>et al.</i>	Exxon	Polyolefins/sulfonated rubber	Processability, impact strength
13.	4,181,644	1980	M. H. Lehr	B.F. Goodrich	CPVC/SBS	Impact strength
14.	4,196,116	1980	W. R. Haaf, <i>et al.</i>	GEC	PPO/EPDM/SB	Processability, flame retardancy, impact strength
15.	4,226,961	1980	G. S. Motz	GEC	PET/PC/aromatic polyester carbonate	Molding transparency
16.	4,233,409	1980	C. W. Bulkley	Monsanto	ABS + 4 rubbers	Low T. ductility
17.	4,239,799	1980	A. S. Weinberg, <i>et al.</i>	W. R. Grace	PVC2/rubber	Processability, O ₂ -barrier
18.	4,239,859	1980	C. R. Miller	Shell	PS/SB	Stiffness—impact balance
19.	4,242,470	1980	W. P. Gergen, <i>et al.</i>	Shell	Nylon/ABA	Impact strength
20.	4,243,764	1981	J. F. Rudd	Dow	PC/ABS	Impact strength, heat resistance
21.	4,243,769	1981	E. G. Pritchett	Natl. Dist.	SAN/EVA	Compatibilization to improve impact and aging resistance
22.	4,247,661	1981	R. M. Herman, <i>et al.</i>	B.F. Goodrich	EPR or EPDM/PP	High melt strength
23.	4,251,644	1981	R. K. Joffrion	Copolym. Rubber	EPM or EPDM/polyesters or polyamides	Compatibility to improve impact, tensile strength, toughness, flexure, etc.
24.	4,251,645	1981	G. Humme, <i>et al.</i>	Bayer A.	PVC/SAN	Low temperature toughness, processability, stability
25.	4,251,646	1981	W. S. Smith, Jr.	Exxon	PP/EPDM/EPR	Modulus, tensile, and elongation at yield
26.	4,255,322	1981	R. M. Kopchik	Rohm and Haas	PVC/polyimide	Transparent blend with high-distortion temperature and impact resistance
27.	4,255,531	1981	H. A. Arbit	Mobil	PPMS/PE	Cross-linkable by electron beam to provide heat resistance and insolubility
28.	4,258,145	1981	R. F. Wright	Phillips	ABA/EPDM/PP	Ozone and solvent resistance, high-temp. hardness
29.	4,264,747	1981	C. F. Paddock	Uniroyal	SAN/SEBS	Weather resistance, impact strength
30.	4,272,431	1981	H. A. J. Schepers	Stamcarbon B.V.	EPDM/PPB	Processability, tensile strength
31.	4,273,893	1981	K. A. Karim, <i>et al.</i>	Gulf Oil	LDPE/PIB/EVA	Heat sealing
32.	4,283,502	1981	P. N. Richardson	DuPont	Nylon/polyolefinanhydride	Nucleation of crystallisation
33.	4,284,734	1981	C. E. Chaney	ARCO	HIPS/PU	Impact resistance, moldability

tion of properties, and extending the use of more expensive engineering polymers are of particular importance.

Scrap Re-Use

A. For years, a large volume of scrap from wire insulation, containing primarily PVC and HDPE, was used as a landfill. A process was developed in which the metal-free scrap, with compatibilizer and filler, was used to generate high-quality material to be used (up to 60 percent) as a core in a multilayer co-injection molding process (43).

B. Uniformly mixed scrap of PS and PE was converted into biaxially oriented sheets with properties similar to those of impact-modified polystyrene.

C. In the UK and Japan, the "Reverzer" process was developed for re-use of municipal mixed plastics scrap. According to Mitsubishi Petrochemicals (44), who developed the Japanese process, a mixture of PE, PP, PS $\leq$ 20 percent, ABS and PVC $\leq$ 50 percent, with up to 50 percent sand, sludge, fibers, or paper, can be molded into stakes, drums, containers, etc. The process in-

cludes: pulverisation, drying, mixing, and injection molding.

D. A Canadian processor discovered a source of contaminated PVC scrap. Blending it with ABS resulted in a superior product. The material was sold with a substantial profit, even after the inefficient compounding added 18 ¢/lb to the price.

The Canadian Waste Materials Exchange, located at the Ontario Research Foundation in Mississauga, Ontario, publishes a monthly list of waste materials available in Canada. The March 1981 listing contains over 1,300 tons/month of plastics scrap available for re-use (45).

Modification of Properties

A. Rigid PVC was modified by the addition of 5 percent poly(acrylonitrile-co-butyl acrylate) (30 percent AN, 70 percent BA). Impact strength was improved by a factor of nine and the thermal stability by 30°C (46). Since the material was nonflammable, had good impact strength and improved thermal stability, it

could be considered as a substitute for ABS/PVC blend, which sells for about 30 ¢/lb more.

B. PET/Nylon blends were investigated recently (47-51). On the basis of these results, a commercial trial was conducted. It was found that extrusion of the blend required about 50 percent lower pressure on the die and resulted in much smoother product with better dimensional control and improved mechanical properties. Since the compounding costs, in this case, were minimal, and since, in addition, the scrap ratio was reduced, the overall profitability of the operation has been improved.

Extending the Properties

To this group of cases belong all the blends containing Nylon, polyesters, polycarbonate, etc., mixed with PE or PP. Due to the approximately three-fold price differential of these resins in respect to polyolefins, "dilution" with PE or PP may bring down the cost of the material. A representative of this class is "Zytel—super tough Nylon"—a blend of Nylon-6,6 with an elastomer having a range of outstanding properties: impact strength, insensitivity to moisture, chemical and heat resistance, easy to use in composites, good surface, etc. (52).

CONCLUSIONS

Cost effectiveness of polymer blending is a complex balance of properties, market demands, and opportunities. It is estimated that more than half Pbl/Pal are manufactured by small processors and compounders to meet a specific market demand/opportunity. As knowledge regarding blend preparation and properties expands, the use of these materials will certainly accelerate.

Blending in the rubber industry is a common, accepted method of achieving the desired performance. To achieve a similar level of acceptance with thermoplastics, significant progress in R/D in these materials will be required. There will always be place in Pbl for the small manufacturer. However, true progress in this domain will demand a higher level of sophistication in the process and composition and their control. Better alloying methods and equipment will have to be developed to control the morphology of the resulting product.

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NOMENCLATURE

- PPO = poly (2,6-dimethyl-1,4 phenylene oxide)
 PS (HIPS) = polystyrene; (high-impact PS)
 PE (LDPE, HDPE, CPE) = polyethylene; (low-density PE, high-density PE, chlorinated PE)
 PP = polypropylene
 PVC(CPVC) = poly(vinyl chloride); (chlorinated PVC)
 ABS = acrylonitrile-butadiene-styrene plastics
 PC = polycarbonate
 PSF = polysulfone
 PET = poly(ethylene terephthalate)
 PBT = poly(butylene terephthalate)
 PPS = poly(phenylene sulfite)
 PTFE = poly(tetra fluoro ethylene)
 PMMA = poly(methyl methacrylate)
 IPN = interpenetrating polymer networks
 SIN = simultaneous interpenetrating networks
 IEN = interpenetrating elastomeric networks
 AA = acrylic acid
 PBR = polybutadiene rubber
 EPR = ethylene propylene rubber
 EPDM = ethylene-propylene terpolymers
 SAN = styrene-acrylonitrile copolymer
 SBS (SB) = styrene-butadiene tri-block (di-block) polymer
 SIS = styrene-isoprene tri-block polymer
 EVA = ethylene/vinyl acetate co-polymer
 PIB = poly(isobutene)
 PDMS = poly(di-methyl siloxane)

- PVC2 = poly(vinylidene chloride)
 ABA = tri-block polymer
 PPMS = poly(p-methyl styrene)
 PPB = propylene-ethylene block polymer
 PU = polyurethane
 SEBS = styrene-ethylene-butylene-styrene block polymer

Discussion

K. C. Frisch. I would like to comment on the patents regarding the blends. I wonder what keywords you used. I did not see in your table some patents I know by Bayer and Mitsubishi. They may be filed under the application, not under "polyblends." This certainly makes it difficult to find them. However, you are absolutely right about the very startling trend.

L. A. Utracki. The computer program uses keywords like polymer blends, SIN, IPN, and their synonyms. Initially, it also searched through "polymer composition" but, since over 95 percent of the selected patents did not have anything to do with polymer blends, we narrowed the search to blends, alloys, and IPNs. Of course, the program searches through a number of data bases.

K. C. Frisch. May I suggest that you get in touch with Sperling. He has brought out a book where there is a very useful patent index; he may be useful.

L. A. Utracki. Yes, thank you very much.

G. Bhatt. When you talked about the multiflight extruders, did you mean the barrier-screw types?

L. A. Utracki. No, these are extruders with a very short, "fat," screw having L/D = 5 with three to six separated flights. Inside the barrel, in front of the screw, there is a barrier disc with an adjustable gap, which provides very high shear zone. The screw provides primarily the melting action. The mixing occurs mainly in the gap zone. The advantage of this device is the very short residence time.

L. St-Pierre. When you listed advantages of blending, you did not stress some important improvements of the processing condition. One of the primary consideration, which went to Noryl, was the lowering of the processing temperature. Coming down from 195°C was very important. When you are looking through the industrial polymers, see how many of them are processed around 100°C. For this reason, even Lexan, processed around 142°C, is not liked. The processing temperature was a very important consideration in formulating Noryl.

L. A. Utracki. You are right. The improvement of processability is one of the most important aspects of blending—e.g., rigid PVC.

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